National Institute for Public Health
and the Environment
Ministry of Health, Welfare and Sport

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RIVM Report 2015-0095

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Colophon

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This investigation has been performed by order and for the account of the Ministry of Infrastructure and the Environment and the Ministry of Economic Affairs, within the framework of the projects ‘Verkenning en Evaluatie gewasbescherming’ and ‘Beoordelingsmethodieken Toelating Gewasbeschermingsmiddelen’.

This is a publication of:
National Institute for Public Health and the Environment
P.O. Box 1 | 3720 BA Bilthoven
The Netherlands
www.rivm.nl/en

Synopsis

Evaluation of the Dutch leaching decision tree with the substances bentazone, MCPA and mecoprop

The leaching of bentazone, MCPA and mecoprop to groundwater was assessed using the new proposals for evaluating sorption and degradation studies (Boesten et al. 2015). The three substances are weak acids, showing pH-dependent sorption behaviour in soil. The evaluation led to large corrections for the sorption endpoint, K_{OM}, derived for individual studies. Consequently, the curve describing sorption as a function of soil pH changed, indicating lower sorption over the relevant pH range. None of the available Freundlich exponents passed the reliability check.

Using the improved interpretation procedures for sorption and degradation experiments revealed that several usages of the substances did not comply with the threshold limit for leaching when assessed at both Tier 1 and Tier 2 of the decision tree on leaching. The assessments did not reveal shortcomings in the decision tree itself. It is recommended that the improved interpretation procedures for sorption and degradation experiments are used for deriving endpoints for future substance leaching evaluations.

Keywords: degradation, drinking water, plant protection products, risk assessment, sorption

Publiekssamenvatting

Evaluatie van de beslisboom voor uitspoeling van bentazon, MCPA en Mecoprop

Evaluatie Beslisboom Uitspoeling Gewasbeschermingsmiddelen naar grondwater

Sinds 2004 wordt een beslismodel (beslisboom) gebruikt om te beoordelen in welke mate een gewasbeschermingsmiddel uitspoelt naar het grondwater. Uit een evaluatie van het RIVM, het College voor de toelating van gewasbeschermingsmiddelen en biociden (Ctgb) en onderzoekinstituut Alterra blijkt dat de beslisboom goed werkt en *state of the art* is. Wel laten de stofgegevens waarmee wordt gerekend te wensen over. Om de kwaliteit van het grondwater te waarborgen moeten deze gegevens zorgvuldiger worden afgeleid.

Drinkwaterbedrijven hebben gevraagd om het beslismodel te evalueren, omdat zij betwijfelen of het grondwater afdoende wordt beschermd. In grondwaterbeschermingsgebieden gelden extra strenge normen voor het gebruik van gewasbeschermingsmiddelen. In grondwater worden soms restanten van gewasbeschermingsmiddelen teruggevonden. Dit betreft voornamelijk stoffen die inmiddels zijn verboden. Ze zijn zeer waarschijnlijk in het verleden gebruikt en door de jaren heen in de ondergrond onvoldoende afgebroken.

Het blijkt dat een aantal stoffen sneller door de bodem wordt getransporteerd dan op grond van de huidige afleidingsmethodiek wordt verwacht. Hierdoor is er minder tijd beschikbaar voor afbraak in de bodem. Met de huidige afleidingsmethodiek voor de stofgegevens wordt dan een te lage uitspoeling berekend en daardoor te lage concentraties in het grondwater. De onderzoekers hebben voorstellen gedaan voor een zorgvuldiger afleiding van stofgegevens voor het beslismodel. De voorgestelde procedures daarvoor zijn beschikbaar in een ander rapport. Door toepassing van deze procedures worden hogere concentraties voor stoffen in het grondwater voorspeld. Voor de drie onderhavige stoffen kan dat aanvullende beperkingen voor de toelating opleveren, wat leidt tot lagere concentraties van deze middelen in het milieu.

Kernwoorden: afbraak, bestrijdingsmiddelen, degradatie, drinkwater, risicobeoordeling, sorptie

Contents

Summary

Occasionally, residues of plant protection products have been found in groundwater in concentrations above the drinking water threshold level. This led to the question whether the groundwater is protected sufficiently by the procedure laid down in the decision tree on leaching of 2004. Therefore, the decision tree was evaluated by assessing the leaching of bentazone, MCPA and mecoprop to groundwater, using the new proposals for evaluating sorption and degradation studies (Boesten et al. 2015).

The three substances are weak acids, showing pH-dependent sorption behaviour in soil. Applying the new proposals for evaluating fate studies led to large corrections for the sorption endpoint, K_{OM}, for individual studies and consequently for the curve describing the dependency on soil pH. Corrections of more than 50% were found for 9 out of 10 sorption values for bentazone, 7 out of 28 for MCPA and 13 out of 20 for mecoprop.

Applying the proposed quality check for the Freundlich sorption exponent N led to the conclusion that none of the evaluated N values could be considered acceptable. Therefore, the default value of 0.9 was used in subsequent evaluations.

Tier 1 leaching calculations showed leaching concentrations above the drinking water threshold limit for all three substances. Tier 2 calculations for bentazone also showed concentrations above this limit. Using the current approach (FOCUS 2006), calculations for MCPA and mecoprop led to concentrations below the limit except for one mecoprop case with an adjusted half-life. Applying the proposed EFSA (2012) approach resulted in exceedances of the limit for applications after 1 June for MCPA and after 1 September for mecoprop. Calculations with the adjusted half-life for mecoprop resulted in an exceedance for the application in March as well. Calculations for historical applications in October showed exceedances for all three substances.

The evaluation revealed that concentrations above the drinking water threshold limit could have been expected for several uses of the three substances if the new proposals for evaluating sorption and degradation experiments had been applied. Using the new proposals in combination with the current decision tree would probably change some authorisations and ensure better protection of groundwater.

Including data from published literature had no influence on the $DegT_{50}$ endpoint for all three substances. Its inclusion had a negligible influence on the K_{OM}–pH relationship for bentazone (admittedly, the ‘published literature’ consisted of only three K_{OM} values, as measured by the RIVM and Alterra for three Dutch soils). In contrast, the published literature had considerable influence for MCPA and some effect for mecoprop. Adding published data led to an increase of the K_{OM} in the most important part of the K_{OM}–pH curve and is therefore expected to decrease the estimated leaching concentrations of MCPA and mecoprop.

Our simulations for mecoprop and MCPA (applications on a well-developed grass cover) showed that use of the default parameters for wash-off and degradation on plant surfaces as recommended by EFSA (2012) may lead to a considerable increase in evaluated leaching concentrations in comparison with the current approach.

Our GeoPEARL simulations for bentazone showed that GeoPEARL is not suitable for simulating wash-off from plant surfaces. Since GeoPEARL is hydrologically based on only three crops (maize, potatoes and grass), it does not simulate wash-off realistically.

The quality criteria for the Freundlich exponent (which led to the rejection of all reported values for this exponent) have a weak scientific basis. We therefore recommend underpinning or improving these criteria by means of an analysis of the error in this exponent.

The new proposal for interpreting indirect batch sorption studies, i.e. using a default correction factor of 10% degradation/loss, sometimes appeared overly conservative in the light of other evidence. This 10% is a conservative value based on the requirement in OECD106 (OECD 2000) to achieve at least 90% recovery of the test substance. We therefore recommend performing a literature review on the relationship between the degradation rate in batch systems and the degradation rate in soil or water-sediment studies, which is likely to allow a less conservative approach.

1 Introduction

Assessment of the leaching of plant protection products (PPP) to groundwater has been part of the authorisation process in the Netherlands since environmental factors were explicitly included in the risk assessment procedures. In the late 1980s and early 1990s it became clear that protecting groundwater as a source of drinking water is the specific protection goal of the assessment procedure. This has been laid down in both the Dutch law on pesticides and related guidance (WGB 2007; Van der Linden et al. 2004).

The principles of the current leaching assessment procedure were laid down in the 'new decision tree on leaching' (Van der Linden et al. 2004), while many practical aspects are covered in the leaching models PEARL and GeoPEARL (Leistra et al. 2001, Tiktak et al. 2000, Tiktak et al. 2003) and leaching scenarios (FOCUS 2000, FOCUS 2009). The assessment follows a tiered approach (Figure 1-1), where Tier 1 is fully harmonised with procedures at the European level and Tier 2 and Tier 3 are more specific to the Netherlands. In all tiers, it is assessed whether the concentrations in groundwater under realistic worst-case conditions exceed the threshold limit for PPP and relevant metabolites in drinking water. The decision criterion in Tier 2 is more explicitly defined as follows: 'the annual average concentration in the groundwater at 1 m depth should not exceed the drinking water threshold level in at least 90% of the potential area of use.' Tier 3 considers transformation in the groundwater between 1 m and 10 m depth and the above criterion should be met at 10 m depth. A stricter criterion is applied for PPP intended to be used within groundwater protection areas.

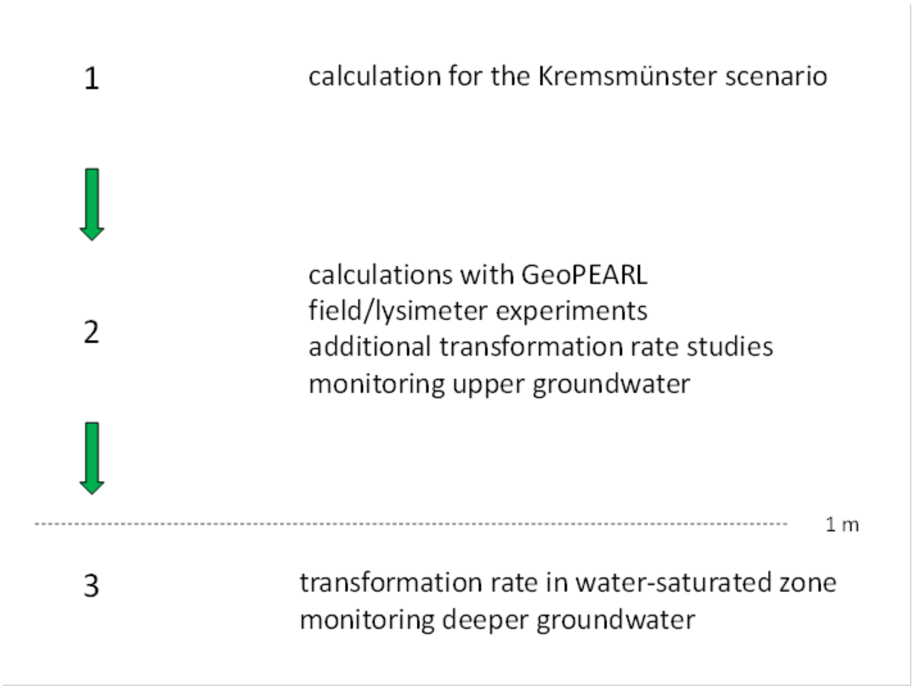


Figure 1-1 Simplified representation of the decision tree on leaching

Drinking water companies and provinces in the Netherlands monitor groundwater (and other environmental compartments) for the occurrence of active substances and metabolites of PPP. Occasionally, residues have been found in concentrations that are above the drinking water threshold level (see for example Van der Linden et al. 2007, Arts et al. 2006). This led to the question whether groundwater is sufficiently protected by the procedure laid down in the new decision tree (Van der Linden et al. 2004). The Ministries of Infrastructure and the Environment (IenM) and Economic Affairs (EZ) therefore initiated a project in order to examine whether the decision tree on leaching of PPP and related metabolites adequately meets the specific protection goal. The research is not to be seen as validation of the decision tree because the correct functioning of the decision tree was not checked against independently derived (monitoring) data, of which the position (ranking) on the cumulative probability density function with respect to leaching is known.

Tier 3 of the decision tree was not evaluated because (1) this tier is only exceptionally used in risk assessment, and (2) it would require a considerable amount of time to determine the representativeness and ranking of the monitoring wells on the cumulative probability density function. This was not considered to be an efficient use of the resources of the workgroup.

At the start of the project, it was considered impossible to establish the representativeness of the wells with sufficient certainty, as past usage patterns, i.e. at the time of infiltration, cannot usually be reconstructed adequately. Consequently, Tier 3 of the decision tree was excluded from this evaluation.

The initial phase of the project identified the PPP substances that are found most frequently in groundwater and are still on the market, as these were considered to be the most worthwhile substances to use in the assessment. The working group identified these as bentazone, MCPA and mecoprop. Substances found in groundwater but taken off the market because of a negative decision with regard to leaching were considered not suitable for testing the decision tree, as, in theory, they would fail to meet the leaching criterion (Boesten et al. 2011). The next phase of the project revealed a number of methodological issues with regard to important input variables in the leaching assessment: the degradation and sorption parameters. The working group decided to address those issues first and recommended several changes in the interpretation of sorption and transformation experiments as well as in the parameters for use in leaching assessments (Boesten et al. 2011).

In the last phase of the project, the working group addressed the basic question: ‘Is the decision tree fit for purpose?’, applying the changed methodologies developed in the earlier phase. The results of this phase are reported here. As deriving pesticide fate characteristics appeared to be critical, the derivation of this data is described separately for each of the test substances (see Chapters 2–4 and the accompanying workbooks). A study of the relevant dossiers and published literature revealed several weaknesses in the proposed methodologies and led to the decision to revise them slightly or describe them more clearly and explicitly. This led to an update of the 2011 report (see Boesten et al. 2015). Conclusions as to whether the decision tree sufficiently meets the specific protection goal of safeguarding the drinking water function of groundwater are given in Chapter 5.

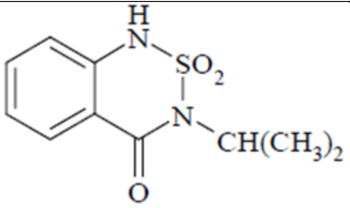
2 Bentazone

2.1 General information on bentazone

This section provides general information on and the physicochemical properties of MCPA according to the currently agreed List of Endpoints on bentazone (European Commission 2000).

The physicochemical properties of bentazone needed for simulation with PEARL are listed in Table 2-1.

Table 2-1 Physicochemical properties of bentazone (European Commission 2000).

Chemical name (IUPAC)	3-isopropyl-(1H)-2,1,3-benzothiadiazin-4-(3H)-one-2,2-dioxide
Molecular formula	C10H12N2O3S
Structural formula	
Molar mass	240.3
Saturated vapour pressure	0.00017 Pa at 20 °C
Solubility in water	pH 3: 490 mg/L at 20 °C
Dissociation constant	pK_a = 3.3

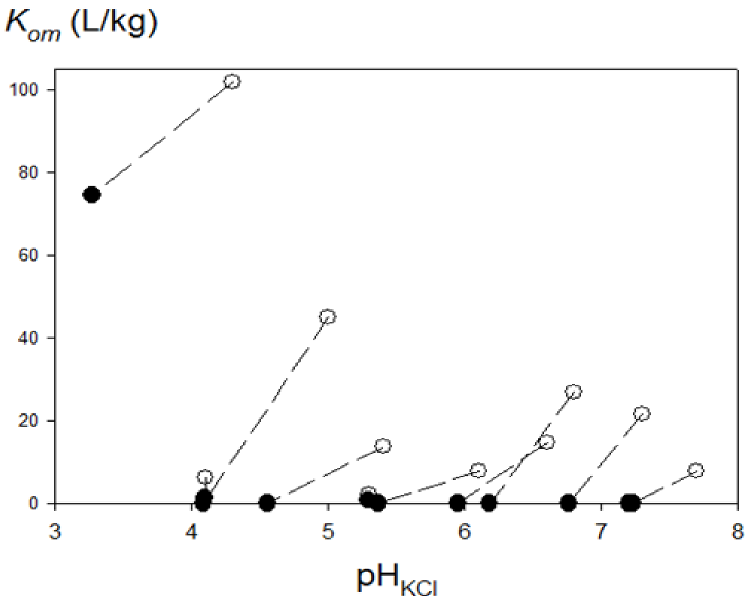
2.2 Sorption

2.2.1 *Batch and TLC studies*

Eight batch sorption values were available from Ctgb dossiers (Ctgb 2002, Ctgb 2003b); these were supplemented by three batch adsorption values taken from sorption studies by the RIVM and Alterra. All these values were established using the indirect method, i.e. the sorption constant was calculated from the decrease in concentration in the liquid phase. The table in the accompanying workbook on bentazone shows the correction procedures for the K_{OM} and pH and their results. (www.rivm.nl/bibliotheek/rapporten/2015-0095Bentazone_sorption_data.xlsm) OECD106 (OECD 2000) prescribes not using the indirect method for determining the sorption constant when the decrease in concentration in the liquid phase is less than 20%. The decrease in concentration in nearly all the dossier studies did not comply with the OECD106 requirement, but as the studies were performed before 2000 this was not used as a deselection criterion. Figure 2-1 shows the original data points together with the corrected ones. The pH values of all the data points from the monograph (ID 1–8) were corrected because the method of the pH measurement was not reported. Figure 2-1 indicates that the correction for the possible 10% degradation had a very large effect on the estimated values; of the ten values shown, seven were corrected to zero. Combination of the workbook with Figure 2-1B shows that the measurements by Boesten and van der Pas (2000) at pH_{KCl} = 5.3 and by Loch et al. (1985) at pH_{KCl}

= 4.1 resulted in non-zero K_{OM} values even after correction. Thus it is likely that the zero K_{OM} values for $pH_{KCl} < 5.5$ obtained from the monograph are underestimations of the true K_{OM}. We therefore propose to discard all zero measurements from the monograph for $pH_{KCl} < 5.5$ (i.e. ID 2, 4 and 7).

A



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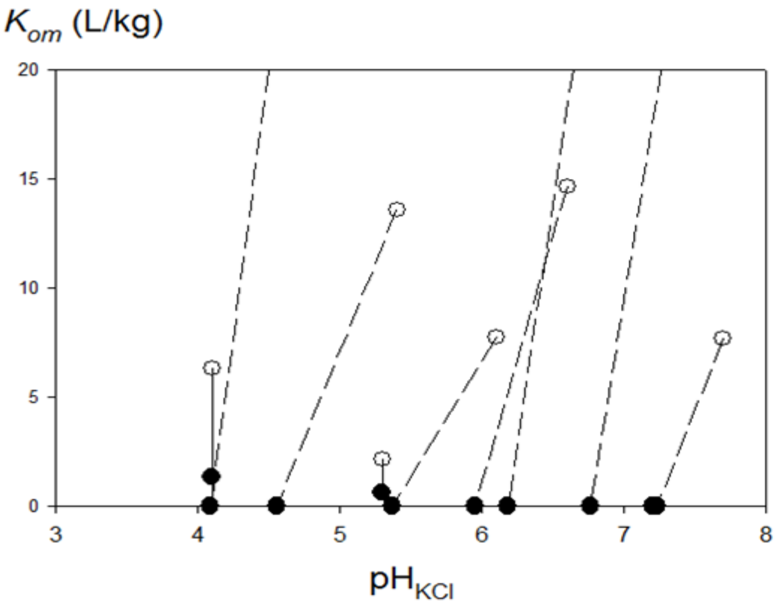


Figure 2-1 K_{OM} values for bentazone as measured in batch studies as a function of pH. Open circles are uncorrected K_{OM} values as a function of measured pH. Closed circles are corrected K_{OM} values as a function of pH_{KCl}. The lines connect uncorrected and corrected pH–K_{OM} pairs. Parts A and B differ only with respect to the scale of the vertical axis.

In view of the large uncertainties in the K_{OM}–pH relationship and the few K_{OM}–pH data pairs left, the soil TLC studies by Abernathy and Wax (1973) were also analysed. These authors report for all their 12 soils that the R_F was 1.0 (‘bentazone moved with the water front on each of the duplicated soil plates, thus achieving an R_F value of 1.0 in the soil–water system’). They provided the chromatogram of one of these studies (Pittwood soil) in their figure 2. We assumed that the centre of mass of the peak was located at the largest width of the radioactivity spot. This resulted in R_{TLC} = 0.95. On the basis of this limited information, we assumed that the R_{TLC} of these 12 soils ranged between 1.0 and 0.95. K values were therefore estimated using R_{TLC} = 0.95 with Eqn 28 of the report with $\theta = 0.3$ and $\rho = 1.0$ kg/L, as recommended in the report. The K values for R_{TLC} = 1.0 are of course 0.

As described in section 3.5 of Boesten et al. (2011), the concentration in the liquid phase of the TLC study has to be estimated on the basis of applied mass and the extent of the solute dot at the end of the experiment. From figure 2 of Abernathy and Wax (1973) we estimated a surface area of the dot of about 2 cm^2. The authors report that they applied 2 µL of a solution with a radioactivity concentration of 0.01 µCi/µL (‘0.01 mCi/mL’). This is a radioactivity of 0.02 µCi. They report elsewhere in the paper a molar radioactivity of 3 Ci/mol (‘2.99 mCi/mmol’). So this 0.02 µCi corresponds to 0.007 µmol bentazone, which is about 1.7 µg of bentazone. So the bentazone concentration in the 2 µL of solution was about 0.8 µg/µL, which is 800 mg/L. The layer was 1 mm thick. So the volume of the solute dot at the end of the experiment was about 0.2 cm^3 and the total concentration in the soil in the solute dot becomes 1.7 µg/0.2 cm^3, or about 10 µg/cm^3, which is 10 mg/L. Using a volume fraction of water of 0.6 (as recommended in the report) and a sorption coefficient of zero, this gives a concentration in the dot (c_{st}) in the liquid phase of 16.67 mg/L. Using Eqn 25 of the report with a Freundlich exponent of 0.9 gives for c_{st} = 16.67 mg/L that K_F is 1.32 times K. This was used in estimating the K_F corresponding to R_{TLC} = 0.95.

It can be expected that the bentazone concentration in the liquid phase at the start of the experiment was an order of magnitude higher because the spot was much smaller; this would have led to a higher c_{st}, and thus to a lower K_F when using Eqn 25.

The pH_{H2O} values as measured by Abernathy and Wax (1973) were converted to pH_{KCl} values with Eqn 34a of Boesten et al. (2011). Abernathy and Wax (1973) used a soil:solution ratio of 1:1, whereas Eqn 34a is based on pH measurements in systems with soil:solution ratios of 1:2 to 1:5. Therefore Eqn 34a may have led to too low pH_{KCl} values in the low pH range (e.g. the pH_{H2O} of 4.6 at a soil-solution ratio of 1:1 would probably have been higher if measured at a soil:solution ratio of 1:5 (Kissel et al. 2004). Therefore, we decided to average the pH_{H2O} and pH_{KCl} values to obtain a more realistic estimate of the true pH_{KCl}.

Figure 2-2 shows the combined data sets of the batch and TLC studies, giving only the K_{OM} values of the TLC studies based on R_{TLC} = 0.95; it should be kept in mind that these values may be zero except for the one for the Pittwood soil (at pH = 6.1 in Figure 2-2). As discussed before, all zero batch measurements from the monograph for pH_{KCl} < 5.5 (ID 2, 4, 7) were discarded. Considering all the TLC data in Figure 2-2, only the K_{OM} derived from the Pittwood soil (0.246 L/kg at pH = 6.1) has added value because the uncertainty in the other TLC values is too large. Given that the K_{OM} for this Pittwood soil is a lower limit because of the limited contact time between soil and liquid phase in TLC studies, we propose to ignore the zero K_{OM} values from the batch studies at corrected pH values of 5.95 and 6.19 (ID 8 and 3) because of the uncertainty in the correction of these K_{OM} values. So only the studies ID 1, 5, 6, 9, 10, 11 and the Pittwood soil study are further considered.

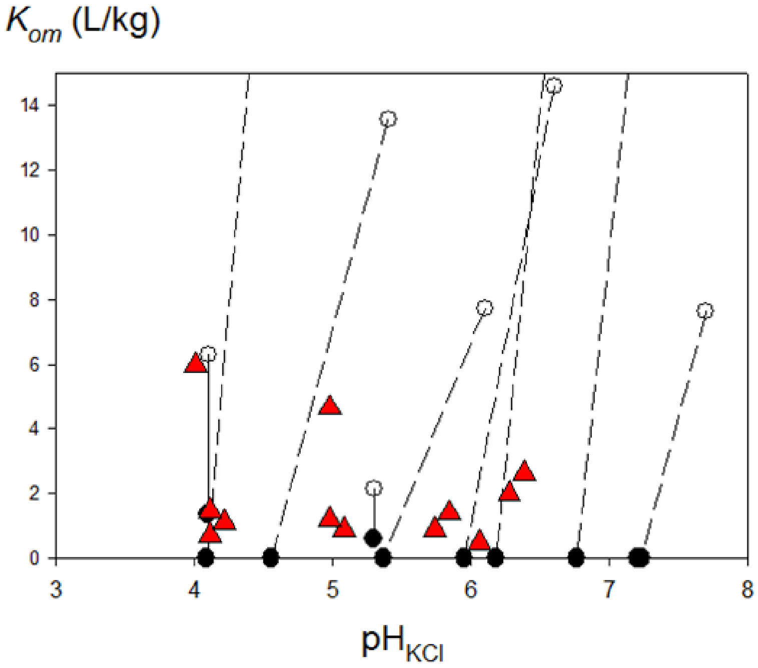


Figure 2-2 The batch data points (circles) and lines of Figure 2-1B plus K_{OM} values of bentazone based on TLC studies (triangles) by Abernathy and Wax (1973). K_{OM} values were calculated assuming R_{TLC} = 0.95. The pH values are averages of pH_{H2O} and the pH values corrected to pH_{KCl} because the correction procedure overestimates the pH shift to lower values. A photograph of the TLC plate was available only for the TLC study at pH = 6.1 (Pittwood soil).

2.2.2 *Soil column studies*

The data in Table 2-2 was extracted from a 1990 Dutch summary authorisation report. All studies were of soil columns 30 cm in length, with a water layer of 20 cm and a leaching time of 2 days.

Table 2-2 Characteristics of the soil column studies of bentazone. The silty sand and the loamy sand were assumed to have the same volume fraction of liquid. The pH_{CaCl2} values and the organic matter content are taken from a personal communication by A.M.A. van der Linden based on information in another dossier.

Nr	Name of soil	% leached	Source	Volume fraction of liquid at -10 cm	pH_{CaCl2}	Organic matter (%)	Organic carbon (%)
1	Sand 2.1	99	BASF (1974a)	0.34	6.2±0.7	?	1.23
2	Sand 2.1	100	BASF (1974b)	0.34	6.2±0.7	?	1.23
3	Loamy sand 2.2	91	BASF (1974a)	0.34	5.8±0.3	?	2.26
4	Loamy sand 2.2	100	BASF (1974b)	0.34	5.8±0.3	?	2.26
5	Sandy loam 2.3	100	BASF (1974a)	0.38	6.3±0.4	?	1.02
6	Sandy loam 2.3	95	BASF (1974b)	0.38	6.3±0.4	?	1.02
7	Silty sand	86–94	BASF (1972)	0.34	?	1.4	
8	Sandy loam	73–88	BASF (1972)	0.38	?	5.3	

These studies were simulated using the analytical solution of Jury and Roth (1990) of the convection–dispersion equation for a semi-infinite soil column. This is strictly speaking not correct because the actual soil column had a length of 30 cm. However, this analytical solution was compared to a numerical solution for a column of 30 cm with a constant θ of 0.34, a dry bulk density of 1.5 kg/L, a dispersion length of 2.5 cm, a linear sorption coefficient of 0.06 L/kg, a $DegT_{50}$ of 1000 d and 200 mm water percolation in 2 days. The numerical solution was based on the PEARL model and the thickness of the numerical compartments was 1 cm. Both the numerical and the analytical solutions showed leaching of 91% of the dosage under these circumstances. Therefore, the analytical solution was considered sufficiently accurate.

The only input parameters besides the sorption coefficient are the volume fraction of liquid (θ), the dry bulk density and the dispersion length. The dry bulk density was set at 1.5 kg/L. The solution uses the product of the dry bulk density and the sorption coefficient, so if the dry bulk density is overestimated by 10%, the sorption coefficient will be underestimated by 10%. The dispersion length was set at 2.5 cm – based on the review by Vanderborght and Vereecken (2007) – but a calculation was also made for a dispersion length of 2.0 cm.

The soil columns are freely draining. This will lead to a matric potential of about 0 cm at the bottom of the soil column and of -30 cm at the top of the soil column at the end of the leaching process. During the leaching, it can be expected that matric potentials are closer to zero than this -30 cm. FOCUS (2000) provides estimates of moisture contents at matric potentials of -10, -100 and -333 cm. It was assumed that θ at a matric potential of -10 cm is a defensible estimate of the θ during the leaching process. The values in Table 2-2 show that the estimated θ values were either 0.34 or 0.38.

As a basis for the estimation of the sorption coefficient, the sorption coefficient was calculated as a function of the percentage leached for both θ = 0.34 and θ = 0.38. Figure 2-3 shows that the sorption coefficient decreases as the percentage leached increases (as would be expected) and that the percentages leached for a given sorption coefficient are higher for sand (θ = 0.34) than for sandy loam (θ = 0.38). The figure shows an additional calculation with a dispersion length of 2 cm. This differed only slightly from the calculation with the dispersion length of 2.5 cm. The sorption coefficient for the respective experiments was estimated from the relationships shown in Figure 2-3 (dispersion length of 2.5 cm). Table 2-3 shows four sorption coefficients below zero, one equal to zero and three above zero ranging from 0.03 to 0.12 L/kg, together indicating no to weak sorption. The sorption coefficients below zero may be realistic because bentazone may occur as anion and its movement may be enhanced by anion exclusion.

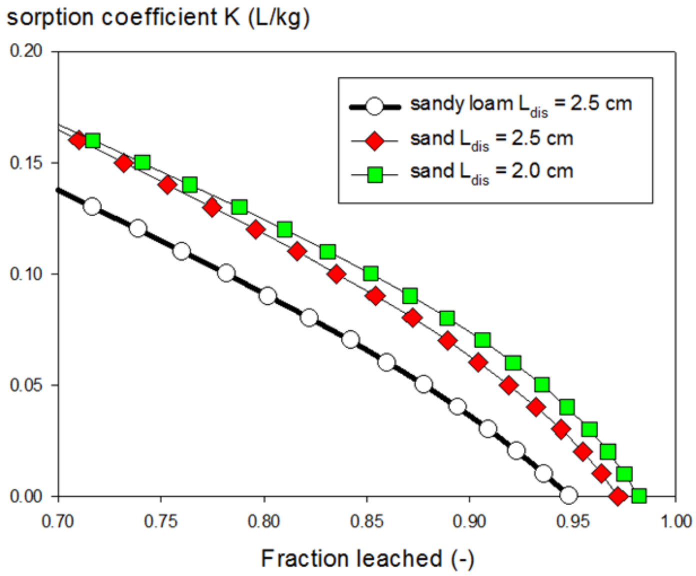


Figure 2-3 The sorption coefficient as a function of the fraction leached from a soil column. Calculations for sand were with a volume fraction of liquid of 0.34 and calculations for sandy loam were with a volume fraction of liquid of 0.38.

Table 2-3 Sorption coefficients of bentazone estimated by inverse modelling from soil column experiments based on percentage leached.

Nr	% leache	Estimated sorption coefficient (L/kg)
1	99	<0
2	100	<0
3	91	0.06
4	100	<0
5	100	<0
6	95	0
7	86–94	0.03–0.09
8	73–88	0.05–0.12

The soil column studies 7 and 8 in Table 2-3 were of no use because the pH of the soils was unknown. So there is one relevant study left with a sorption coefficient above zero (0.06 L/kg). In this study 91% of a dose of 1.92 kg/ha leached with a water layer of 200 mm. Assuming that this leaching occurred in half of the water layer, this gives a leaching concentration of $0.91 \times 192 \text{ mg/m}^2 / 0.1 \text{ m} = 1747 \text{ mg/m}^3 =$ 1.747 mg/L. The Freundlich coefficient can then be calculated by Eqn 25 of Boesten et al. (2011) with c_{st} = 1.747 mg/L and N = 0.9. This gives a Freundlich coefficient of 0.063 L/kg. The organic carbon content was 2.26% (Table 2-2), so the organic matter content was 3.9%, which gives a K_{OM} of 1.63 L/kg.

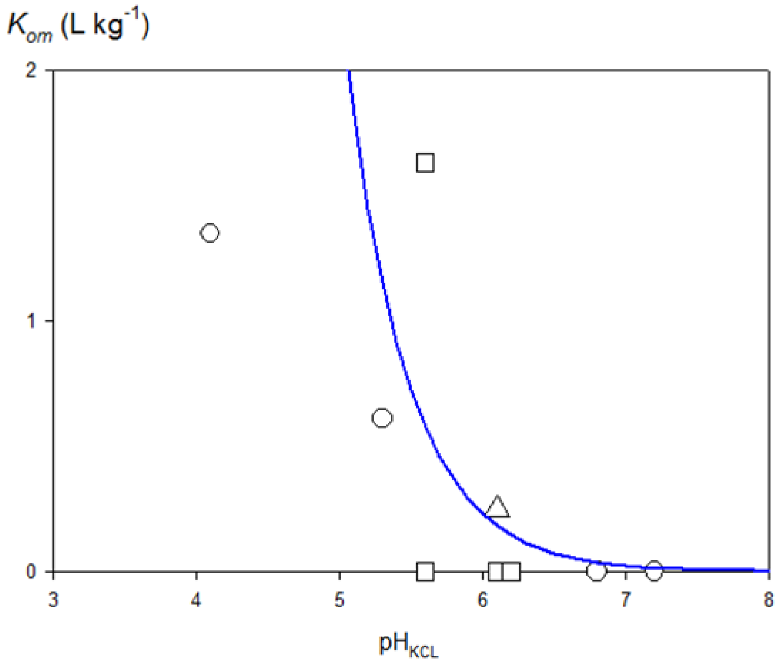
2.2.3 *Combination of batch, TLC and soil column studies*

Figure 2-4 shows all previously accepted results of batch and TLC studies plus the results of the relevant soil column studies. The upper part shows that all measured K_{OM} values for pH_{KCl} values above 4 are close to zero. The lower part zooms in on these low values and shows considerable scatter. This scatter is probably caused by the low accuracy; for example, the K_{OM} of 1.63 L/kg is based on leaching of 91% of the dose whereas the K_{OM} of zero at pH_{KCl} = 6.1 is based on 95% leaching (column study nr 6 in Table 2-1). These slight differences in leaching percentages may be responsible for this scatter. Therefore, there were no reasons to reject any of the data points shown in Figure 2-4.

All accepted K_{OM}–pH pairs are listed in Table 2-4. These were fitted to Eqn 31 of Boesten et al. (2011) using the software package GraphPad Prism with a pK_a of 3.3, based on the List of EndPoints (LoEP), and a molar mass of bentazone of 240.8. In the first fit the ΔpH was fitted. However, this resulted in a ΔpH of -3.4, which is not within the acceptable range given in Boesten et al. (2011). Therefore, ΔpH was fixed to the closest limit value (-0.2) in the second fit. Figure 2-4 shows that the second fit resulted in an acceptable description of the measurements. The resulting parameters were $K_{OM,acid}$ = 183 L/kg and $K_{OM,anion}$ = 0.0 L/kg. It would have been desirable to show also the 95% confidence intervals of the fit in Figure 2-4, as for example in Figure 3-4, but this appeared not possible with a fixed ΔpH.

Table 2-4 Selected combinations of K_{OM} and pH_{KCl} values for bentazone.

Type of study	ID	pH_{KCl}	K_{OM} (L/kg)
batch	1	6.8	0
batch	5	7.2	0
batch	6	3.3	74.61
batch	9	5.3	0.61
batch	10	4.1	1.35
batch	11	7.2	0
TLC	1	6.1	0.25
column	1	6.1	0
column	2	6.1	0
column	3	5.6	1.63
column	4	5.6	0
column	5	6.2	0
column	6	6.2	0



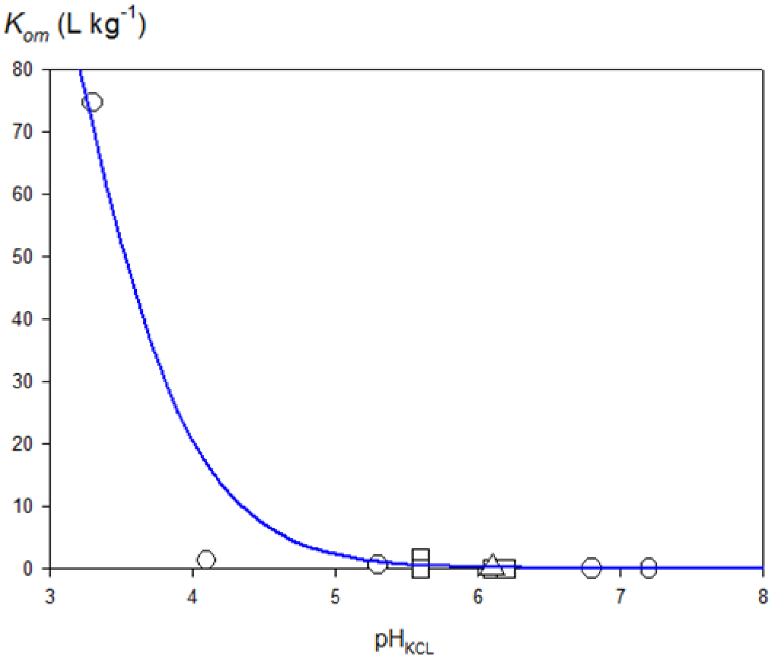


Figure 2-4 The data points selected for fitting for bentazone and the fit of the K_{OM}*–pH equation to these points assuming* $\Delta pH = -0.2$ *(*$K_{OM,acid} = 183$ *L/kg,* $K_{OM,anion} = 0.0$ *L/kg). Circles are batch studies, the triangle is a TLC study, and squares are column studies.*

The effect of including data from published literature – i.e. the three K_{OM} values measured and reported by the RIVM and Alterra – was assessed. These values were 0.61, 1.35 and 0.25 L/kg, as shown in Table 2-4. The set of data from Table 2-4 without these three K_{OM} values was again fitted to Eqn 31 of Boesten et al. (2011) using GraphPad Prism. The resulting fitted line was very close to the line shown in Figure 2-4. The only difference in the fitted parameters was that the $K_{OM,acid}$ was 192 L/kg instead of the 183 L/kg. So the conclusion is that adding the data from RIVM and Alterra studies has almost no influence on the resulting K_{OM}–pH relationship.

The values of the Freundlich exponent N are considered unreliable because the Φ values in all batch studies were below 0.8.

2.3 Degradation

In view of the time constraints within the project, the assessment of the $DegT_{50}$ of bentazone was limited to the application of the current guidance to five field dissipation studies and to combining this with an available data set of laboratory $DegT_{50}$ studies assessed by Ctgb (2002). The new guidance elements considered were (i) the assessment of the total amount of bentazone in the soil profile as described by Boesten et al. (2015) and (ii) the assessment procedure of the $DegT_{50}$ as described by EFSA (2014). The consequences of these limitations for the leaching assessment will be discussed later.

2.3.1 Laboratory studies

Ctgb (2002) made a selection of available reported $DegT_{50}$ values from laboratory studies excluding (i) studies from period 1972–1974, (ii) studies on soils having undergone repeated application of bentazone, and (iii) studies whose results were not reported in sufficient detail. After this selection, 27 $DegT_{50}$ values of bentazone measured in laboratory studies on topsoils at 20 °C were left. Their geometric mean was 26 d and the standard deviation of the natural logarithms of the $DegT_{50}$ was 0.8; the minimum was 4 d and the maximum was 99 d. No moisture correction of these $DegT_{50}$ values was reported by Ctgb (2002). We did not apply further quality checks to this data because these were superseded by the results of the field studies, as will be shown hereafter. We did check whether the $DegT_{50}$ of the laboratory studies showed a pH dependency. Figure 2-5 shows that there is some indication that the $DegT_{50}$ increases with pH but the scatter is very large. The correlation coefficient of the data in Figure 2-5 was found to be 0.2, which indicates no significant correlation for 27 values. So we concluded that the $DegT_{50}$ of bentazone is not dependent on the pH of the soil.

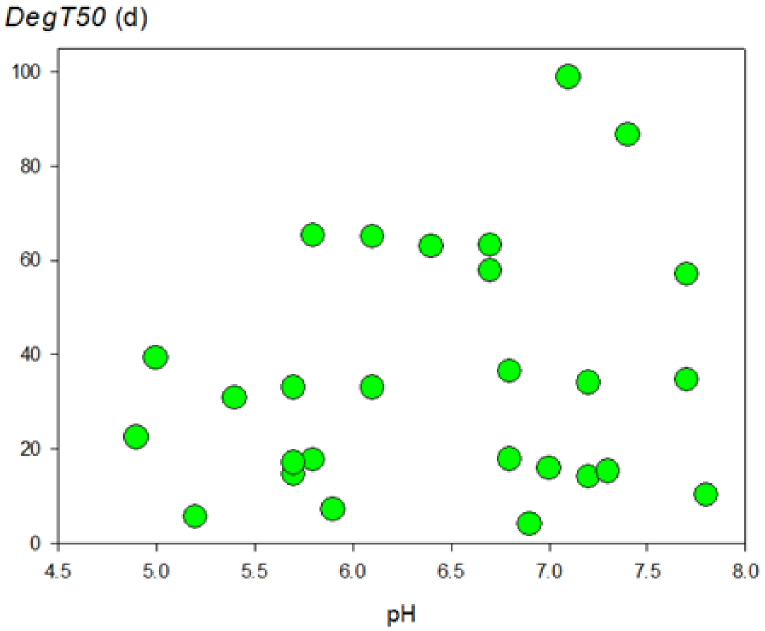


Figure 2-5 The DegT$_{50}$ of the 27 laboratory studies at 20 °C as a function of pH (type of pH unknown)

2.3.2 *Field studies*

2.3.2.1 Introduction

Hesse and Schepers (1991) and Schepers and Hesse (1991) report in total five field persistence studies at the locations Holzen, Stetten, Limburgerhof, Havixbeck and Goch-Nierswalde. Gottesbüren and Platz (1999) provided additional information about these studies. The pH$_{CaCl2}$ of these soils ranged between 5.9 and 7.1. Furthermore, BASF provided daily meteorological data (air temperatures and rainfall) for these studies.

In Holzen and Stetten, bentazone was applied to bare field plots measuring at least 6 x 24 m. Application was done with knapsack sprayers with a boom width of 2–3 m. Nozzles were 22–34 cm above the soil surface. The soil was kept bare during the experiment by mechanical weed control. Soil was sampled with an auger with a diameter of 5 cm. At each sampling time, soil was sampled at five spots within a 3 x 3 m sub-plot; the distance between the spots was at least 50 cm. The soil of corresponding layers from the five spots was mixed, so for a certain layer only one soil sample was available for chemical analysis. Thus no information was available on variability within the fields.

In Limburgerhof, Havixbeck and Goch-Nierswalde, bentazone was applied to bare field plots of at least 50 m^2. Application was done with knapsack sprayers in Limburgerhof and Havixbeck and with a sprayer on a small car in Goch-Nierswalde. The soil was bare during the experiment and weeds were controlled mechanically if necessary. Soil was sampled with an auger with a diameter of 5 cm. At each sampling time, soil was sampled at seven spots randomly distributed over the field; the distance between the spots was at least 50 cm. The soil of corresponding layers from the seven spots was mixed, so for a certain layer only one soil sample was available for analysis. Thus no information was available on variability within the fields.

Initial recoveries of the dose were generally low: 79% for Havixbeck, 65% for Goch-Nierswalde, 52% for Limburgerhof and Stetten, 21% for Holzen. The reason for this is not clear.

The available concentrations in the sampled soil layers were converted to mass per surface area (areic mass) assuming a dry bulk density of 1.5 kg/L for all layers. These areic masses were summed to give the total amount of bentazone in the soil profile using the rules for handling values below the LOQ, as described by Boesten et al. (2015). Time step normalisation was applied, as described by FOCUS (2006), using a Q10 of 2.58.

Boesten et al. (2015) recommend labelling field $DegT_{50}$ values as potentially unreliable if these are based on fewer than 20 samples at each sampling time. The five field experiments were based on 5-7 samples, so these $DegT_{50}$ values have to be considered potentially unreliable. We will discuss the consequences of this in Section 2.3.3.

The guidance by EFSA (2014) contains two flow charts for the assessment of the $DegT_{50}$ from field persistence studies. The first considers fitting to the Single First Order (SFO) or Double First Order in Parallel (DFOP) models after applying time step normalisation; if these fits are not successful, the guidance suggests switching to the second flow chart, which is based on fitting to the Hockey Stick (HS) model (see EFSA (2014) for details). These flow charts are the basis of the assessments in the following sections.

2.3.2.2 Field experiment at Havixbeck

The first field experiment considered was the one at Havixbeck (Schepers and Hesse 1991). Table 2-5 shows the calculated total amounts of bentazone and cumulative rainfall as a function of time and normalised time.

Table 2-5 Remaining amounts of bentazone in soil and cumulative rainfall as a function of time in the field experiment at Havixbeck.

Time (d)	Normalised time (d)	Cumulative precipitation (mm)	Areic mass (mg/m^2)
0	0	8	117.6
14	6.69	24	64.9
28	16.89	36	17.6
57	39.17	77	10.5
98	74.15	162	1.8

Following EFSA (2014), it has to be checked whether the field decline (after time step normalisation) can be described with SFO after eliminating the data points before 10 mm rain has fallen. EFSA (2014) recommends basing the check on the quality criteria of FOCUS Kinetics (FOCUS 2006): a visual assessment of goodness of fit combined with a χ^2 test for the goodness of fit and a t-test to evaluate the confidence of the parameter estimates. The SFO fit resulted in an initial areic mass of 140 mg/m^2, a DegT$_{50}$ of 6.0 d (95% confidence interval 4–17 d) and a χ^2 error of 16%. The t-test for the DegT$_{50}$ was passed at a level of 4.8% and the χ^2 error was very close to the acceptance trigger value of 15% suggested by FOCUS (2006). However, the fit in Figure 2-6 was considered visually unacceptable because the calculated decline is faster than the measured decline for the last two data points.

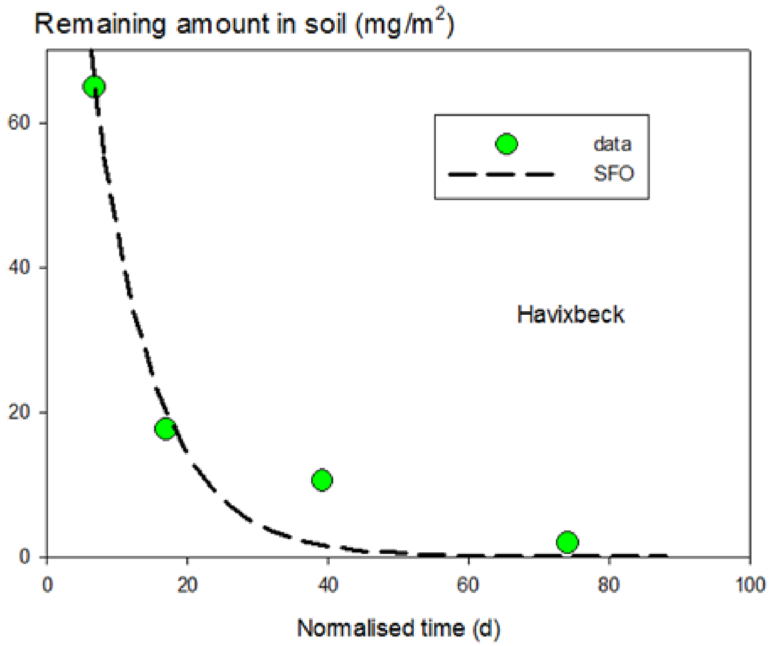


Figure 2-6 Fit of the SFO model to the remaining amount of bentazone in the soil profile as a function of normalised time at Havixbeck. Points are measurements with cumulative rainfall above 10 mm and the line is the SFO fit.

The next steps according to EFSA (2014) are to fit the DFOP model to the whole data set and to check whether the g-parameter of the DFOP model (i.e. the fraction in the fast-degrading compartment) is less than 0.75. The fit resulted in g = 0.95, which was too large. EFSA (2014) then recommends fitting the HS model to the whole data set and to check whether cumulative rainfall was more than 10 mm at the breakpoint time. The breakpoint time was 16.9 d so there had indeed been more than 10 mm of rain at this time (Table 2-5). The next step is to check whether the fit is acceptable by visual assessment and assessment of the χ^2 error. Figure 2-7 shows that the fit was visually acceptable. The χ^2 error was 7%, which is below the trigger of 15% of FOCUS (2006) and therefore acceptable. The next step is to check whether the slow rate coefficient (k_2) of the HS model is significantly larger than 0. This was not the case: the t-test showed a probability of 18%. EFSA (2014) recommends using expert judgement in such a case; as indicated by EFSA (2014), the worry is that the k_2 value is too low and that the resulting DegT$_{50}$ (which was in this case 19 d) is longer than the DegT$_{50}$ derived from the available laboratory studies. This is not the case in view of the geometric mean DegT$_{50}$ of 26 d of the laboratory studies. Therefore, the DegT$_{50}$ of 19 d was considered an acceptable endpoint of the Havixbeck field study.

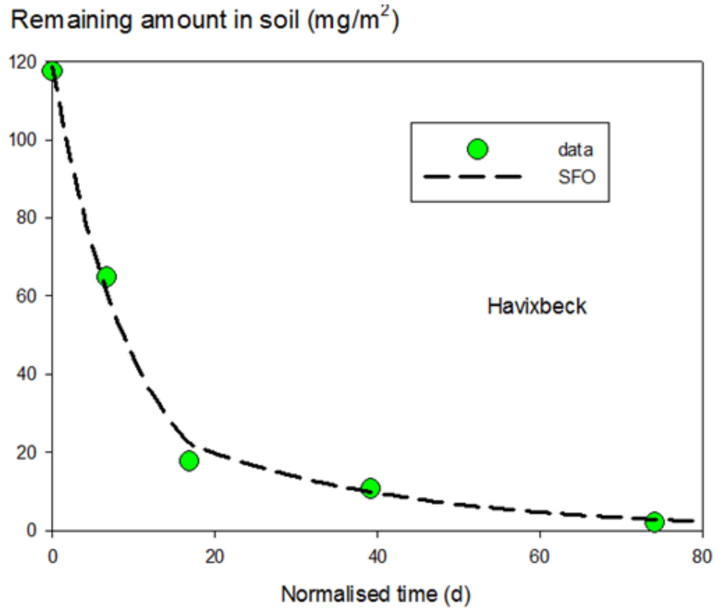


Figure 2-7 Fit of the Hockey Stick model to the remaining amount of bentazone in the soil profile as a function of normalised time at Havixbeck. Points are the measurements and the line is the fit.

2.3.2.3 Field experiment at Holzen

The second field experiment considered was Holzen (Hesse and Schepers 1991). Table 2-6 shows the calculated total amounts of bentazone and cumulative rainfall as a function of time and normalised time.

Table 2-6 Remaining amounts of bentazone in soil and cumulative rainfall as a function of time in the field experiment at Holzen.

Time (d)	Normalised time (d)	Cumulative precipitation (mm)	Areic mass (mg/m^2)
0	0	5	31.4
7	4.9	22	31.3
14	10.2	26	19.1
30	19.6	72	18.7
51	35.7	182	0.8

The first step is to check whether SFO gives an acceptable fit based on normalised time and after eliminating data points before 10 mm of cumulative rain. The fit was considered visually more or less acceptable (Figure 2-8). The fitted DegT$_{50}$ was 12 d. The χ^2 error was 18%, i.e. only slightly higher than the trigger value of 15% from FOCUS (2006). As described by FOCUS (2006, p. 116), the 15% trigger value is not an absolute cut-off. The t-test for the DegT$_{50}$ showed a significance level of 6.3%. FOCUS (2006) considers significance levels above 10% to be unacceptable and recommends further discussion and justification for levels between 5% and 10%. We consider a significance level higher than 5% unjustifiable because the decline was based on only four data points.

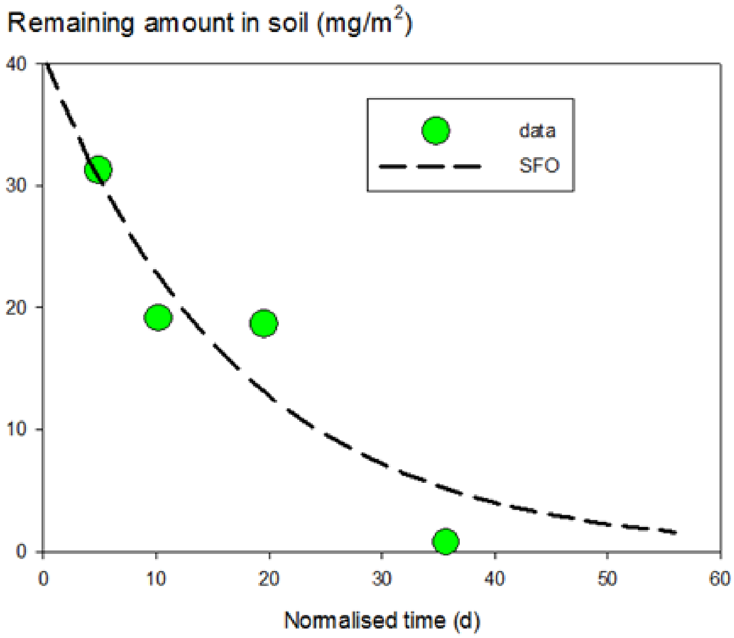


Figure 2-8 Fit of the SFO model to the remaining amount of bentazone in the soil profile as a function of normalised time at Holzen. Points are measurements with cumulative rainfall above 10 mm and the line is the SFO fit.

Based on EFSA (2014) the next step is to fit DFOP to the whole data set (i.e. the points shown in Figure 2-8 plus the remaining amount of 31.4 mg/m^2 at the start). This resulted in a g-value of the DFOP model of 0.85, which is considered unacceptable by EFSA (2014). The next step is to fit the HS model to the whole data set and to check whether 10 mm of rain has fallen at the breakpoint time. The breakpoint time was 23 d so the criterion of 10 mm of rainfall was fulfilled (Table 2-6). The fit was considered acceptable based on a χ^2 error of 15% and visual inspection (Figure 2-9). However, an assessment of the accuracy of the slow phase rate coefficient k_2 was impossible because this was based only on the last two data points (see Figure 2-9). In this case, EFSA (2014) indicates that expert judgement has to be applied. Figure 2-9 shows that the fit did not generate a meaningful result because it indicates acceleration of the degradation process between the penultimate and the last data points.

This assessment of the $DegT_{50}$ for Holzen indicates that the guidance as described by EFSA (2014) will usually lead to non-acceptance of the study in cases where the SFO fit is considered unacceptable because there is no clear bi-phasic decline.

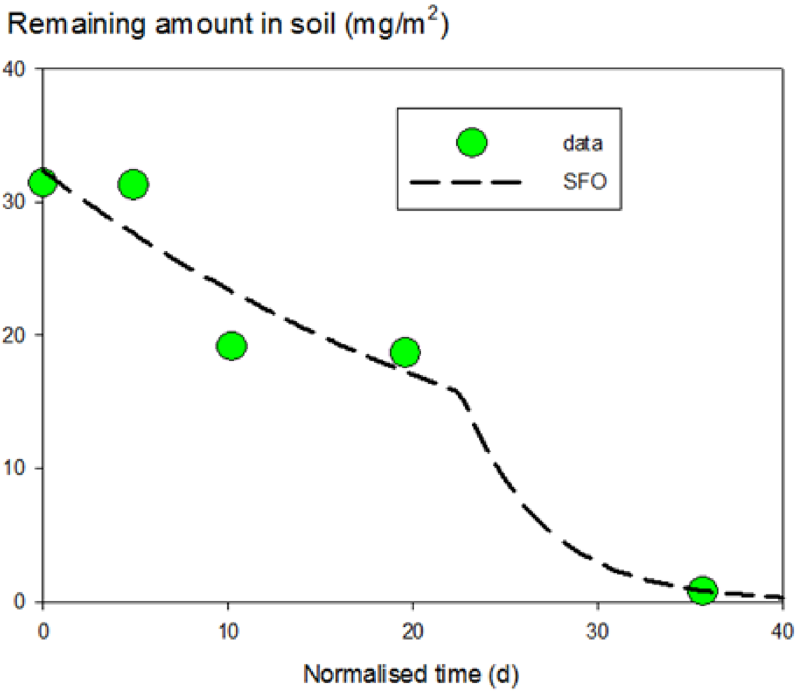


Figure 2-9 Fit of the Hockey Stick model to the remaining amount of bentazone in the soil profile as a function of normalised time at Holzen. Points are the measurements and the line is the fit.

2.3.2.4 Field experiment at Stetten

The next field data set considered is Stetten (Hesse and Schepers 1991). Table 2-7 shows the calculated total amounts of bentazone and cumulative rainfall as a function of time and normalised time.

Table 2-7 Remaining amounts of bentazone in soil and cumulative rainfall as a function of time in the field experiment at Stetten.

Time (d)	Normalised time (d)	Cumulative precipitation (mm)	Areic mass (mg/m^2)
0	0	0	75.7
7	4.48	3	53.0
13	9.41	3	32.0
29	20.98	16	29.9
61	42.87	111	11.0
103	84.51	168	3.1

The first step is to check whether SFO gives an acceptable fit based on normalised time and after eliminating data points before 10 mm of cumulative rain. Figure 2-10 shows that only three data points were left after this elimination and that the SFO fit to these points was visually acceptable. The χ^2 error was 5% and the t-test of the rate coefficient was passed at a significance level of 4%. The resulting $DegT_{50}$ of 16 d was considered acceptable in view of the good fit, although it was based on only three data points.

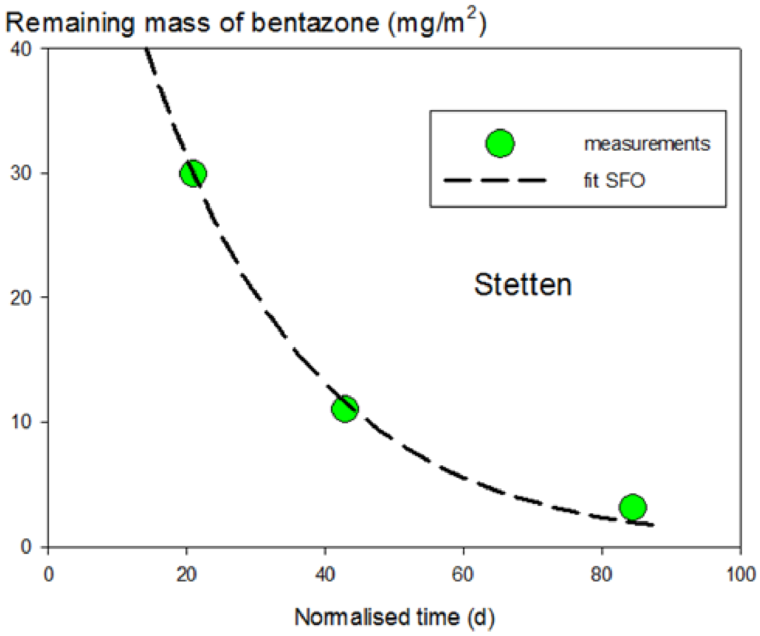


Figure 2-10 Fit of the SFO model to the remaining amount of bentazone in the soil profile as a function of normalised time at Stetten. Points are measurements with cumulative rainfall above 10 mm and the line is the SFO fit.

2.3.2.5 Field experiment at Goch-Nierswalde

Table 2-8 shows the calculated total amounts and of bentazone cumulative rainfall as a function of time and normalised time for the field experiment Goch-Nierswalde.

Table 2-8 Remaining amounts of bentazone in soil and cumulative rainfall as a function of time in the field experiment at Goch-Nierswalde.

Time (d)	Normalised time (d)	Cumulative precipitation (mm)	Areic mass (mg/m^2)
0	0	0	98.8
14	8.4	56	54.5
30	23.8	66	21.7
60	50.9	131	8.6
100	84.0	170	2.3

The first step is to check whether SFO gives an acceptable fit based on normalised time and after eliminating data points before 10 mm of cumulative rain. Figure 2-11 shows that only four data points were left and that the SFO fit to these points was visually acceptable.

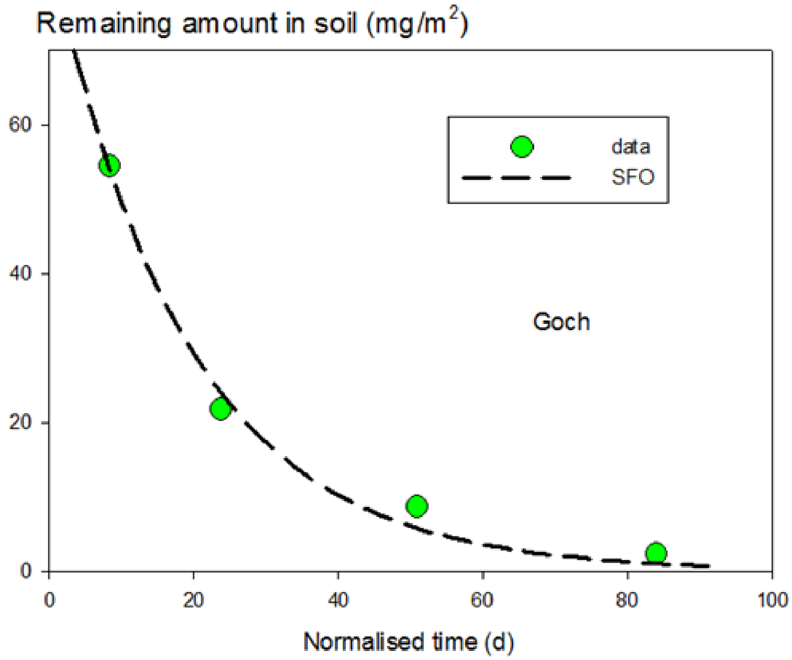


Figure 2-11 Fit of the SFO model to the remaining amount of bentazone in the soil profile as a function of normalised time at Goch. Points are measurements with cumulative rainfall above 10 mm and the line is the SFO fit.

The χ^2 error was 7% and the t-test of the rate coefficient was passed at a significance level of 0.9%. So the resulting $DegT_{50}$ of 13 d was considered acceptable.

2.3.2.6 Field experiment at Limburgerhof

Table 2-9 shows the calculated total amounts of bentazone and cumulative rainfall as a function of normalised time for the field experiment at Limburgerhof. There was a complication with respect to the residues at day 14: in the layer at 37–50 cm depth a residue level of 0.06 mg/kg was measured, whereas the layers at 0–12 cm, 12–25 cm and 25–37 cm contained levels of 0.06, 0.04 and 0.03 mg/kg, respectively. At day 30, residue levels of the 0–12 cm, 12–25 cm, 25–37 cm and 37–50 cm layers were <0.02, 0.02, 0.02 and <0.02 mg/kg, respectively. Schepers and Hesse (1991) considered the value of 0.06 mg/kg at day 14 in the 37–50 cm layer as a contamination because it is inconsistent with the other residue data. We agree because cumulative rain was 30 mm at day 14, so penetration of a significant fraction below 37 cm depth was unlikely. The texture of the soil is loamy sand (16% < 20 µm) so strong preferential flow effects are considered unlikely. Moreover, on day 30 the residue level in the 37–50 cm layer was less than that in the 25–37 cm layer. Therefore, the residue level in the 37–50 cm layer on day 14 was set at <0.02 mg/kg.

Table 2-9 Remaining amounts of bentazone in soil and cumulative rainfall as a function of time in the field experiment at Limburgerhof.

Time (d)	Normalised time (d)	Cumulative precipitation (mm)	Areic mass (mg/m^2)
0	0	1	77.0
14	12.4	30	25.7
30	26.8	59	11.8
60	57.4	130	3.8

The first step is to check whether SFO gives an acceptable fit based on normalised time and after eliminating data points before 10 mm of cumulative rain. Figure 2-12 shows that only three data points were left and that the SFO fit to these points is visually acceptable.

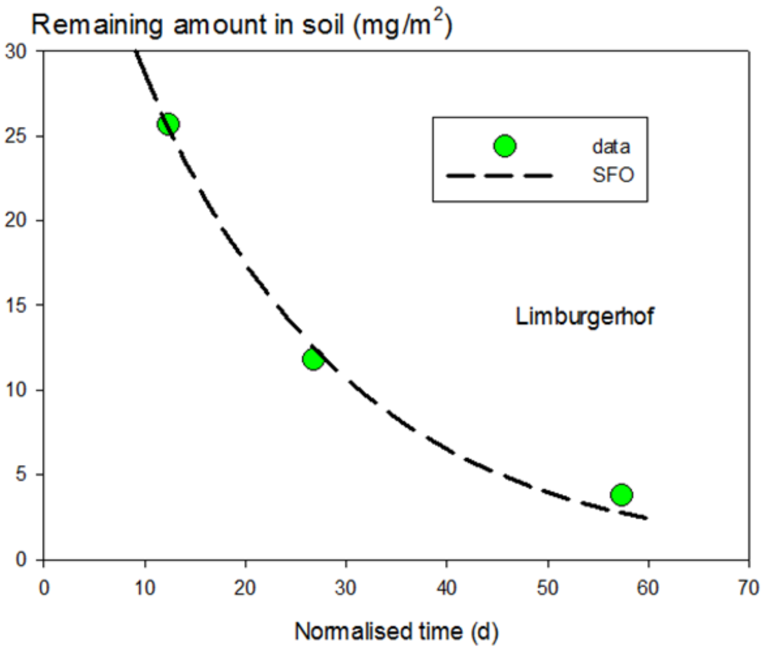


Figure 2-12 Fit of the SFO model to the remaining amount of bentazone in the soil profile as a function of normalised time at Limburgerhof. Points are measurements with cumulative rainfall above 10 mm and the line is the SFO fit.

The χ^2 error was 5% and the t-test of the rate coefficient was passed at a significance level of 4%. So the resulting DegT$_{50}$ of 17 d was considered acceptable.

It should be noted that the rejection of the value of 0.06 mg/kg in the 37–50 cm layer after 14 d (normalised time 12.4 d) was in principle a conservative assumption: a higher value after 12.4 d normalised time would have decreased the estimated DegT$_{50}$ because 14 d is the first data point in Figure 2-12. However, it is not certain that this is a conservative assumption because accepting the value of 0.06 mg/kg might have led to rejecting the SFO fit, thus leading to a bi-phasic fit with DFOP and possibly HS, which could have led to a higher estimated DegT$_{50}$.

2.3.3 *Combination of field and laboratory $DegT_{50}$ values*

EFSA (2014) gives a flow chart for the assessment of the $DegT_{50}$ endpoint if $DegT_{50}$ values from both field and laboratory experiments are available. The principle is that the laboratory $DegT_{50}$ values can be rejected if it is demonstrated that the field $DegT_{50}$ values are significantly lower than the laboratory values. This has to be based on a statistical test with the null hypothesis that the geometric mean $DegT_{50}$ of the laboratory experiments is equal to the geometric mean $DegT_{50}$ of the field experiments. EFSA (2014) provides a calculator for performing this test. The significance level to be used is 25%.

We therefore have 27 laboratory $DegT_{50}$ values with a geometric mean of 26 d and a standard deviation of the natural logarithms of 0.8, and four field $DegT_{50}$ values of 13, 16, 17 and 19 d. The result of the test was that the geometric mean field $DegT_{50}$ of 16 days is indeed significantly lower than the geometric mean laboratory $DegT_{50}$. The significance level appeared to be between 12% and 13%. The flow chart of EFSA (2014) requires further that there be at least four field $DegT_{50}$ values. This requirement is fulfilled, so the $DegT_{50}$ of 16 d is the endpoint of this $DegT_{50}$ assessment, based on the EFSA flow chart.

As described in Section 2.3.2.1, the field $DegT_{50}$s have to be considered potentially unreliable because they were based on only 5–7 soil samples per sampling time. However, the four field $DegT_{50}$s are in a narrow range (13–19 d), and it is considered unlikely that all four field studies resulted in too short a $DegT_{50}$ because of the spatial variability in the measured soil residues: in total 13 soil samples (Havixbeck 3 (Figure 2-7), Stetten 3 (Figure 2-10), Goch-Nierswalde 4 (Figure 2-11) and Limburgerhof 3 (Figure 2-12) from different sampling times were used to fit these $DegT_{50}$s. Therefore, the fact that there were only 5-7 sampling spots is not considered to be a problem.

EFSA (2010) collected a number of data sets of laboratory $DegT_{50}$ measurements with the same substance and a range of soils and found that the standard deviation of the natural logarithms ranged between 0.2 and 0.5. So the value of 0.8 found here is considerably larger than the values found by EFSA (2010). However, the variation in the field $DegT_{50}$s (normalised to 20 °C) is quite small (12–19 d): the standard deviation of the natural logarithms of 13, 16, 17 and 19 d is 0.16. EFSA (2010) reports two standard deviations of $DegT_{50}$ values from field experiments: 0.4 and 0.6, i.e. considerably larger than for the field $DegT_{50}$s of bentazone found here. A possible reason is the quite narrow pH range of the field soils considered (pH_{CaCl2} of 5.9 to 7.1). However, we could not find a correlation with pH in the laboratory studies as shown before.

Scorza Junior and Boesten (2005) performed a field experiment on a Dutch clay soil planted with winter wheat and obtained an inversely modelled field $DegT_{50}$ of 12 d (using a measured Arrhenius activation energy of 74 kJ/mol). This value is close to the field $DegT_{50}$ values reported here, but it is not included in the statistical test because it could not be evaluated in accordance with the EFSA (2014) guidance. The reason is that plant uptake may have played an important role in the dissipation of bentazone.

There is a considerable safety margin in the rejection of the null hypothesis: the actual significance level was 12–13% whereas a level of 25% is required. It is therefore considered unlikely that a further detailed examination of the 27 other laboratory studies would have led to another conclusion of the DegT_{50} assessment.

2.4 Selected usages and assessment

Bentazone is applied to many crops. Two usage patterns were evaluated: (A) usage typical of the period 1980–1990 and (B) current usage.

The selected usages were those expected to have the highest leaching. The usage typical of the period 1980–1990 was assumed to be an application of 1.44 kg/ha to maize on 25 May or the same rate in a series of crops on 15 October (PD 1991). Because the application date of 15 October results in higher leaching concentrations, the application to maize was ignored. On this basis, the usage covering the period 1980-1990 was defined as an application of 1.44 kg/ha to grass grown for seed generation on 15 October.

The highest leaching of bentazone can be expected from the highest dose and from application in autumn. The relevant current usage is application to grass (grown for seed generation) at a rate of 3 L/ha Basagran (i.e. 1.44 kg/ha bentazone). The usage label states that application should take place when the grass seedlings have three to five leaves and not later than 1 October. On this basis, the current usage was defined as an application of 1.44 kg/ha to grass grown for seed generation on 1 October. Calculations were also made for earlier application dates to check the effect of the application date.

In the stage of three to five leaves, the BBCH code used for grass is 10-19, based on the BBCH growth stages for cereals (Lancashire et al. 1991, Meier 2001). For this BBCH code a crop interception of 40% for grass (EFSA 2014) is used for the simulations.

The current approach is to subtract the amount intercepted from the application amount (FOCUS 2000), which implies that interception acts as a sink for the PPP. EFSA (2012) proposes accounting for the dissipation of PPP from leaf surfaces and using 100 m^{-1} for the wash-off factor in combination with a half-life of 10 d for other dissipation processes on the crop canopy, unless measured values are available. The proposed wash-off parameter may lead to a substantial increase in the amount of PPP estimated to reach the soil surface. It was therefore decided to do simulations for both the current approach and the alternative proposed by EFSA. The latter approach is more conservative towards leaching.

The simulations were performed for both Tier 1 and Tier 2 of the decision tree for the usages indicated above. The physicochemical properties are given in Section 2.1 and the sorption and transformation data derived in Sections 2.2 and 2.3. As prescribed, the sorption parameter for bentazone used in the Tier 1 calculations is the $K_{\mathrm{OM,anion}}$. All Tier 1 calculations, i.e. for the current method and the alternative approach, assuming different crop canopy processes, led to concentrations above the threshold limit. Therefore, Tier 2 assessments had to be performed. Table 2-10 shows the results of the calculations for eight application times in respect of current usage and one for the historic usage (application on 15 October), for both the two canopy parameterisations and the two tiers.

Table 2-10 90^{th}-percentile leaching concentrations (µg/L) for different calculation scenarios for bentazone.

Application	Canopy processes according to FOCUS (2000)		Canopy processes according to EFSA (2012)	
	Tier 1	Tier 2	Tier 1	Tier 2
Current, 1 March	43.5	5.3	46.1	5.3
Current, 1 April	44.5	2.6	48.5	2.6
Current, 1 May	46.8	2.2	54.5	2.3
Current, 1 June	42.3	2.7	47.3	3.3
Current, July	42.9	4.2	48.3	5.8
Current, 1 August	49.2	9.9	59.5	15.0
Current, 1 September	59.9	23.3	78.2	35.2
Current, 1 October	70.0	33.6	87.6	33.8
Historic, 15 October	80.2	37.5	105.0	37.9

All simulations result in 90^{th}-percentile leaching concentrations of more than 20 times the acceptability level of 0.1 µg/L. The highest concentration, 35.2 µg/L, is found for the September application with EFSA (2012) canopy parameters.

For the application timing giving the highest concentration (1 September), Figure 2-13 shows the cumulative frequency of the calculated potential leaching concentrations after bentazone application of 1.44 kg/ha to grass with EFSA (2012) canopy parameterisation, and Figure 2-14 shows the geographical variability of leaching concentration. Figure 2-13 shows that the calculated concentration exceeds 0.1 µg/L for the whole area of use for this September application. Figure 2-14 shows that the highest concentrations are calculated for the clay areas in the northern and western parts of the Netherlands, and in the polders in the centre of the country.

The chosen historical application of bentazone results in a higher leaching concentration than the current 1 October application. This is due to the later timing of the application in the year, with higher net precipitation shortly after application.

Table 2-10 shows that setting the canopy parameters to the values recommended by EFSA (i.e. a DT_{50} of 10 days and a wash-off factor of 100 m^{-1}) resulted in 90^{th}-percentile concentrations that are similar to those using the FOCUS approach, which is remarkable. The crop intercepts 40% of the loading, so with the FOCUS canopy approach 40% of the bentazone loading will not wash off to the soil, whereas with the EFSA canopy approach part of the 40% is expected to wash off to the soil. Hence, higher leaching concentrations would be expected from the EFSA approach. The application on 1 October leads to 90^{th}-percentile concentrations of 33.6 µg/L (FOCUS) and 33.8 µg/L (EFSA). Such a small difference seems implausible with a crop interception of 40%. From the results of the simulations, the plot closest to the 90th-percentile concentration was selected for further investigation. For the FOCUS canopy approach, this was plot 4918, where maize was used for the hydrology simulation (leaching concentration of 33.6 µg/L). For the EFSA canopy approach, it was plot 5386, where maize was also used for the hydrology simulation[1] (leaching concentration 33.9 µg/L). For the EFSA approach the next closest plot to the 90th-percentile concentration was the same as the plot closest to the 90th-percentile in the FOCUS approach, i.e. plot 4918 (leaching concentration 33.6 µg/L). Hence, for plot 4918, where all other input is the same, the difference in approach has little effect on the leaching concentration. The mass balance of the canopies of plot 4918 revealed that almost all intercepted bentazone is removed with the harvest. The cropping period of maize is 20 May to 17 October.

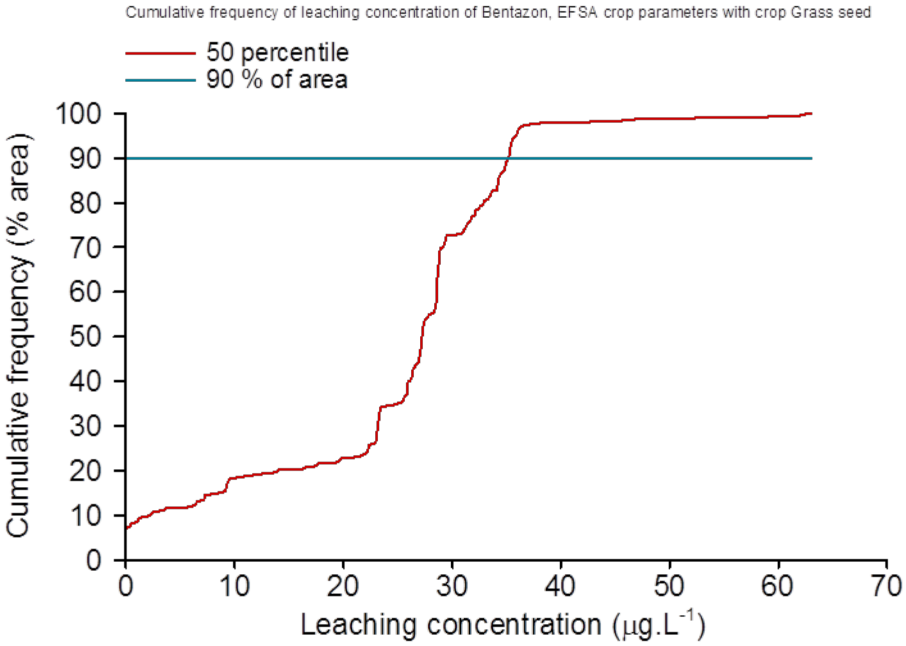


Figure 2-13 Potential leaching concentrations after bentazone application of 1.44 kg/ha on 1 September, with wash-off from leaves (EFSA parameterisation of canopy processes)

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[1] GeoPEARL simulates the hydrology of a plot using crop parameters of the crop representing dominant land use in the plot. Furthermore, each crop is assigned to one of four land uses: grass, maize, potatoes or nature.

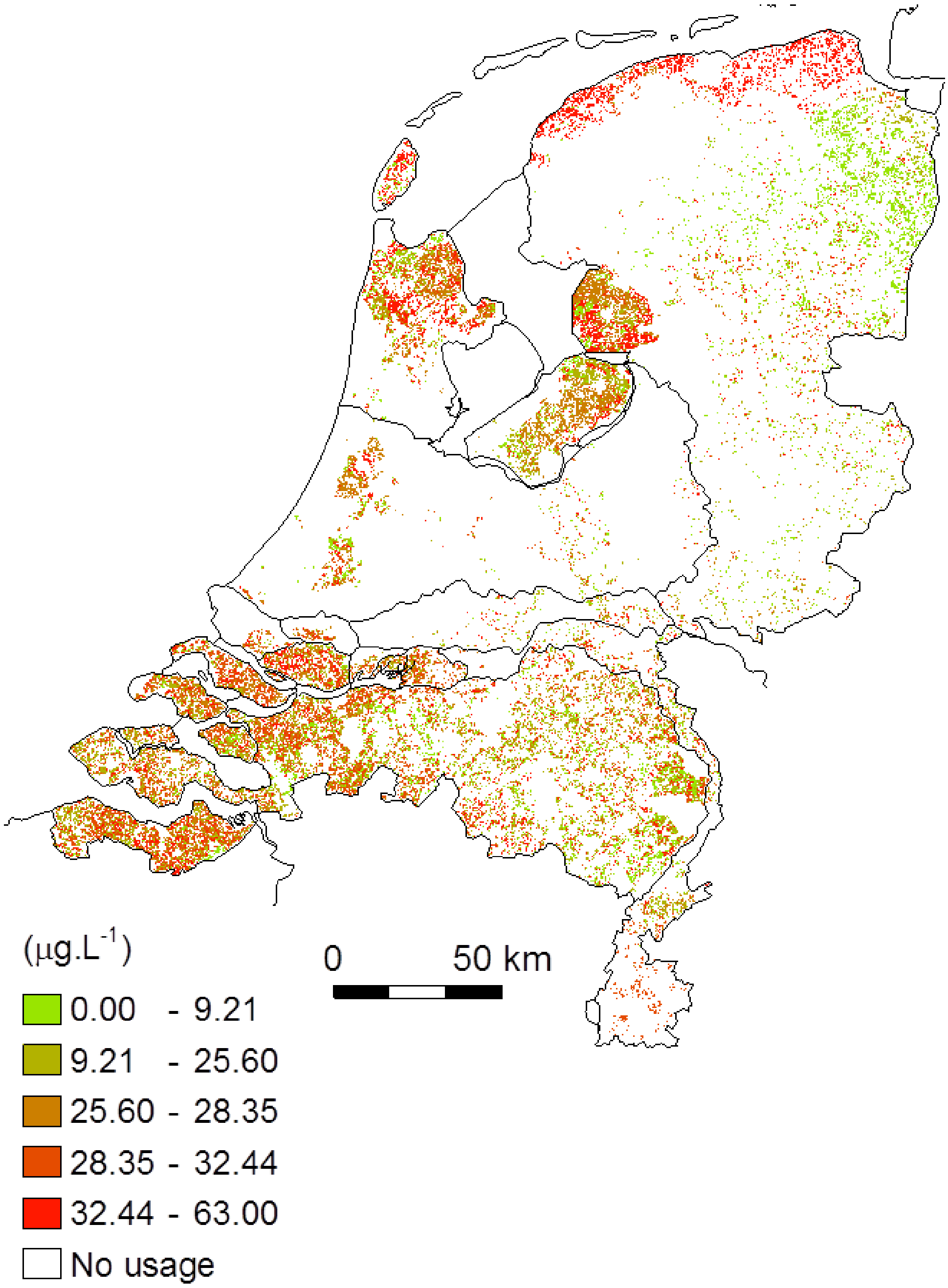


Figure 2-14 Map of bentazone leaching concentrations (50th percentiles) after application of 1.44 kg/ha on 1 September to grass, with wash-off from leaves (EFSA canopy parameterisation)

If all bentazone on the crop canopy washes off, concentrations can be a factor 100%/(100%–40%) higher in the EFSA approach than in the FOCUS approach. Only the August and September applications show higher leaching concentrations with the EFSA approach than with the FOCUS approach. The leaching concentrations from other application timings in the cropping period hardly differ for the two approaches. Hence, the new EFSA canopy parameterisation may not fit with how crops are simulated in GeoPEARL.

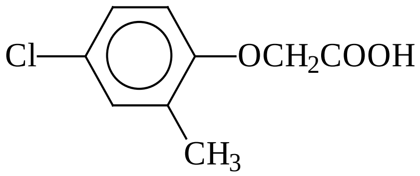
The 90th-percentile concentration of bentazone in groundwater exceeds the drinking water limit of 0.1 µg/L calculated by GeoPEARL for the worst case crop (with respect to leaching), which is grass grown for seed production, using the improved guidance proposed by Boesten et al. (2015) for the determination of sorption and transformation parameter values of bentazone with studies available in the dossier and in published literature.

3 MCPA

3.1 General information on MCPA

This section provides general information on and the physicochemical characteristics of MCPA (see also Table 3-1) according to the List of Endpoints (LoEP) on MCPA (EC 2008).

Table 3-1 Physicochemical properties of MCPA (EC 2008).

Active substance (ISO common name)	MCPA
Chemical name (IUPAC)	4-chloro-*o*-tolyloxyacetic acid
Molecular formula	$C_9H_9Cl0_3$
Molecular mass	200.6
Structural formula	
Vapour pressure (Vp)	4 x 10^{-4} Pa at 32 °C (99.4%) 4 x 10^{-3} Pa at 45 °C (99.4%)
Solubility in water	Solution — Solubility (g/L) at 25 °C pH=1 unbuffered — 0.395 ± 9.1 pH=5 buffered — 26.216 ± 1.403 pH=7 buffered — 293.898 ± 5.329 pH=9 buffered — 320.093 ± 5.945 Purity = 99.4 %
Hydrolytic stability (DT_{50})	^{14}C-MCPA acid was stable to hydrolytic degradation at pH 5, 7 and 9 at 25 °C for 30 days.
Dissociation constant	pK_a = 3.73 (s = 0.07) at 20 °C pK_a = 3.73 (s = 0.00) at 25 °C Purity = 99.8 %

MCPA is slightly volatile and its water solubility is very high for its salts.

3.2 Sorption

A scan of the MCPA dossier and published literature (not an in-depth literature search) revealed a high number of sorption studies. Only studies with unaltered soils, i.e. soils without added material (e.g. peat and ash) that could influence the sorption of MCPA, were taken into consideration. An overview of the studies, with the (not-corrected) sorption constants, is given in Figure 3-1 and the individual values are given in Appendix B. In total, 134 sorption experiments (115 batch values, 14 column values and 5 soil TLC values) were examined. Details on the handling of MCPA column leaching and soil TLC studies are also given in Appendix B.

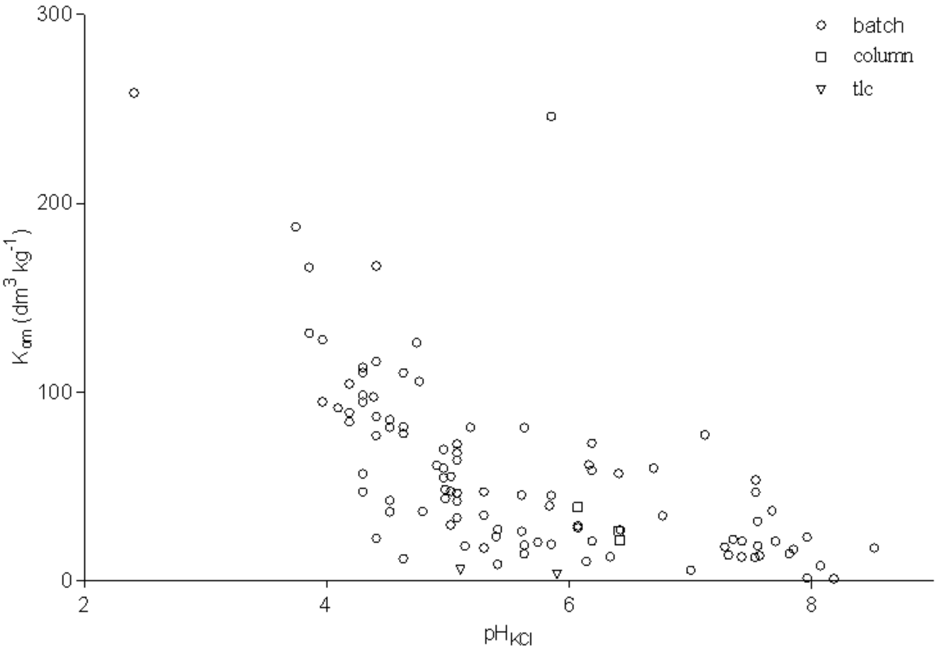


Figure 3-1 Overview of raw sorption data of MCPA. Reported pH values are converted to pH_{KCl} where appropriate, assuming pH_{H2O} when not reported. K_{OM} values are not corrected.

MCPA is a substance whose dissociation status depends on the pH of the soil. As the pK_a of MCPA is 3.73, it is expected that its sorption is also dependent upon the pH of the soil. Sorption constants and pH values are used to derive a sorption curve. In this case, both pH values and sorption constants have to be sufficiently reliable. Studies were assessed for completeness of information and quality of the experiments in order to derive reliable sorption constants and the most appropriate function for the dependency of the sorption on the pH of the soil. pH_{KCl} was chosen to construct the relationship, in line with the soil pH map contained in GeoPEARL.

The selection of reliable values followed a stepped approach. Table B-3 in Appendix B gives the selection step at which values were considered not sufficiently reliable or not fulfilling the requirements of the authorisation assessment procedure. This selection elaborates on the procedure described in section 3.6.3 (step 1) of Boesten et al. (2011). (http://www.rivm.nl/bibliotheek/rapporten/2015-0095MCPA_sorption_data.xlsm)

3.2.1 *Selection of MCPA sorption coefficients*

Step 1: elimination of duplicates and data with insufficient quality
In this step ‘insufficient quality’ is assigned to data with:

- a missing pH value
- a missing sorption constant (K_D, K_F, K_{OC}, K_{OM}), or a sorption constant given as a maximum
- a missing soil:solution ratio

- an incorrect or uncertain calculation method where the basic experimental data is not available (if basic data was available, the sorption data were recalculated)
- an unknown water layer in column studies
- an unknown water flow rate in column studies
- an unknown penetration depth or column length.

Where duplicates (different values reported for the same soil) remained after applying the quality criteria, expert judgement was applied to select the most reliable values. In the three cases where duplicate values remained, the values according to the batch equilibrium method were preferred because the description of the experiments was considered to be more complete.
After this step, 100 values remained: 97 batch, 1 column and 2 TLC values.

Step 2: removal of data with suspected influence of transformation
When the indirect batch equilibrium method is used, prolonged equilibration time may lead to excessively high sorption values because of transformation. According to the indirect method, the difference between the initial and equilibrium concentrations is the basis for the calculation of the sorption. If the transformation is higher than the default limit (10%), the proposed correction based on the minimum recovery of 90% (see Boesten et al. (2011)) may be insufficient. All data obtained in experiments without any sterilisation and an equilibration time of four days or longer was considered to have insufficient quality at this step.
After this step, 60 values remained, including 1 column and 2 TLC values.

Step 3: removal of sediments and soils from below the plough layer
Standard evaluation/assessment considers topsoils only, so values for sediments and subsoils (i.e. soils deeper than 30 cm) were removed from the selection.
After this step, 42 values remained, including 1 column and 2 TLC values.

Step 4: removal of data from soils with low organic matter/organic carbon content.
In soils with low organic matter, sorption onto other surfaces may contribute significantly to the overall observed sorption. It has become common practice not to include sorption constants from soils with low organic matter content (%OM < 0.5, %OC < 0.3) in the calculation of the average sorption constant. Sorption values fulfilling this criterion were removed. The limit values are taken (or derived) from Mensink et al. (2008).
After this step, 40 values remained, including 1 column and 2 TLC values.

OECD106 prescribes not using the indirect method for determining the sorption constant when the decline in concentration in the liquid phase is less than 20%. In nearly 60% (22 out of 37) of the batch experiments remaining after the fourth selection step, the decline in concentration in the liquid phase was less than 20%. It was, however, decided not to use this as a deselection criterion, as many of the experiments were performed before the guideline was published in 2000.

Figure 3-2 gives an overview of the data remaining after the selection procedure as well as the data deselected at the various steps (except data deselected in step 1, as this data was not considered reliable enough for this study).

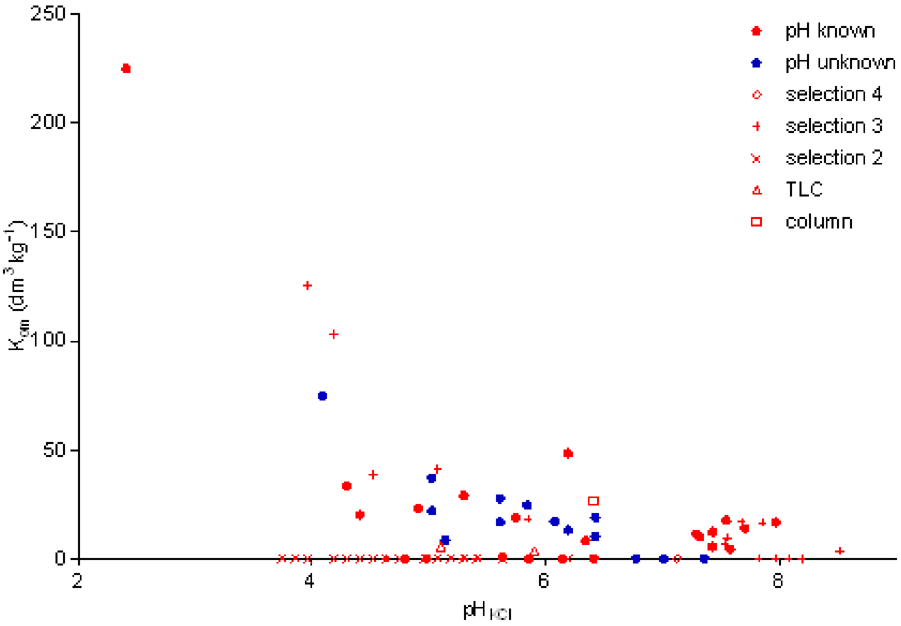


Figure 3-2 Corrected K_{OM} versus pH_{KCl}. Selection 2 – 4 indicate the data points deselected in step 2 – 4 of the selection procedure. pH unknown indicates the points for which the pH measurement method was not stated. The series pH known, pH unknown, TLC and column remained after step 4 of the selection procedure.

All K_{OM} values remaining after the fourth step (see Appendix B) were considered to be reliable enough and belonging to the correct population of sorption values to be used for deriving the function relating the sorption of MCPA to soil pH. However, for 16 experiments the pH measurement method was not stated in the available information. So, for these data points there is uncertainty about the pH. The default when the measurement method is missing is to assume that the measurement method is according to pH_{H2O}, which is conservative because the correction will shift points to the left when figures are converted to pH_{KCl} or pH_{CaCl2} for practically all relevant pH values. The uncertainty in the pH was nevertheless investigated further (see below).

Figure 3-3 gives reported as well as corrected K_{OM} values for the data points remaining after step 4. Because of the number of values remaining after the selection procedure, the graphs presented here deviate from the recommended graphs; a graph with all connection lines between uncorrected and corrected points for both K_{OM} and pH would be illegible. For data with a known pH measurement method, only the correction for K_{OM} is given. (Note that the correction procedure leads to a lower K_{OM} value, but not to a shift in pH.) In Figure 3-3 this can be observed as a vertical shift (always downward). For data points with an unknown pH measurement method, there is a shift to the left because of the default assumption that the method is according to the H_2O method. Reported and corrected data points are connected by dotted lines in Figure 3-3. The largest correction for data points with a known pH measurement method is 48 L/kg, compared with 34 L/kg for data points with an unknown pH measurement method. Based on visual inspection of the graph, there is no reason to deselect the data points with an unknown pH measurement method.

Nearly all corrections are based on default assumptions, as exact information for performing corrections was missing. Only in a few cases was the recovery stated and used in the corrections. The default corrections may, however, be overly conservative. For the following points (numbering corresponds to Appendix B) there is reason to discard the data in the fitting procedure because the correction may be overly conservative:

Data point	Location (blue symbol in Figure 3-3)	Remark
B115	(4.79, 0.0)	The correction is quite substantial (36.6 L/kg) because of a low soil:solution ratio. T4 is in the vicinity at a slightly higher pH value and has a positive value. As TLC values are regarded as minimum values, the correction for B115 might be too large.
B61	(4.98, 0.0)	The correction is substantial (48.3 L/kg). T4 is in the vicinity at a slightly higher pH value and has a positive value. As TLC values are regarded as minimum values, the correction for B61 might be too large.
T4	(5.1, 5.75)	TLC values are regarded as minimum values. There are higher positive values (after correction) from batch experiments in the same pH range.
B31	(5.14, 8.67)	Default pH correction of 0.8 pH units; data points in the neighbourhood are higher.
B1	(5.85, 0.0)	T5 is in the vicinity and has a larger K_{OM} value, so the correction for B1 may be too large.
B57	(5.63, 0.7)	T5 is in the vicinity and has a larger K_{OM} value, so the correction for B57 may be too large.
T5	(5.90, 3.4)	TLC values are regarded as minimum values. There are higher positive values (after correction) from batch experiments in the same pH range.
B55	(6.14, 0.0)	T5 is in the vicinity and has a larger K_{OM} value, so the correction for B55 may be too large.
B3	(6.40, 0.0)	The correction for B3 is quite substantial and C1 (at approximately the same pH) has a larger K_{OM} value, so the correction for B3 may be too large.
B30	(6.67, 0.0)	B30 has an unknown pH measurement method. There are several points with non-zero sorption after correction at higher pH.
B27	(7.35, 0.0)	B27 has an unknown pH measurement method. There are several points with non-zero sorption after correction at approximately the same pH.

Points B53 (6.34, 8.3), B54 (7.57, 4.44) and B56 (7.42, 5.56) were not discarded because the corrections were relatively small and the corrected values were not substantially lower than the uncorrected values of other data in the vicinity, so there was no indication that the corrections were overly conservative.

The remaining points (28 batch and 1 column values, see Table 3-2) were subjected to the fitting procedure. Figure 3-4 gives the resulting curve and the 95% confidence interval for a non-restricted fit (see Table 3-3 for fitted values and their statistics). The fit without constraints led to a pH-shift value outside the acceptable range. Therefore, the fit was repeated, constraining the pH-shift value to -0.2. The resulting curve is also given in Figure 3-4 and the fitted values and statistics are listed in Table 3-3, in column B. The non-restricted fit falls within the 95% confidence interval of the restricted fit, in the entire relevant pH range.

As stated earlier, there are points for which the pH measurement method is unknown and this adds to the uncertainty of the results. It is worthwhile investigating whether a reduction in the uncertainty of the underlying information leads to a better curve. Additional fits were performed in order to assess the influence of the correction for pH measurement method on the sorption curve. Fits were performed for two cases: (1) using all acceptable K_{OM} values, assuming that the unknown pH measurement method was in accordance with the pH_{KCl} measurement method, and (2) using only those acceptable K_{OM} values with a known pH measurement method. Case (1) can be considered as a best case, i.e. non-conservative as higher calculated K_{OM} values are expected in the relevant pH range when there is no shift of values to a lower pH. If the results of such a fit differ substantially from the results of the default approach, it may be worthwhile making further attempts to find the details of the measurement method. For this case, fitted K_{OM} values were 236 L/kg for the acid and 19.1 L/kg for the anion, with the pH shift restricted to -0.2. Confidence intervals were, however, much larger than those reported in Table 3-3. As expected, in the relevant pH range, i.e. pH_{KCl} between approximately 3.5 and 8.5, the curve is indeed above the curve obtained with the standard procedure, so less conservative with respect to predicted leaching. The differences are, however, small. For case (2) it is *a priori* unknown whether the result will be less conservative or not, as a number of values are left out. In a data-rich situation, leaving out uncertain values may lead to more acceptable results. For case (2), fitted K_{OM} values were 236 L/kg for the acid and 14.4 L/kg for the anion, with the pH shift restricted to -0.2. Also in this case the confidence intervals are much larger than those reported in Table 3-3, probably due to the lower number of degrees of freedom. In case (2), a slightly more conservative curve is obtained (i.e. lower sorption values over the range pH4–pH8). The reduction in uncertainty of the input in this case does not lead to lower uncertainty in the fitted sorption parameters. Despite the slightly more conservative result in case (2), the default results are accepted because of the lower uncertainties in the values.

The MCPA dossier evaluated a number of column and TLC studies from published literature, but only two TLC studies and one column study were considered reliable enough for consideration in this study. The two TLC studies were discarded, however, as TLC studies deliver lower limits, and higher sorption values were found in experiments with approximately the same pH.

The dossier contained eight batch sorption results from experiments performed by the notifiers. One of these results was discarded because the soil did not meet the requirement for organic matter content. The corrected values of the seven other experiments were used to fit the pH-dependent sorption equation. This resulted in a $K_{OM,acid}$ of 104 L/kg, a $K_{OM,anion}$ of 4.2 L/kg and a pH shift of 0.75. The resulting curve using these values is below the curve of the restricted fit except in the pH range between approximately 4 and 5.25 (see Figure 3-4). It is expected that, when using this curve for GeoPEARL calculations, the 90^{th}-percentile concentration is above the value when using the result of the fitting on all selected values. This assumption is based on the lower $K_{OM,anion}$ value, which will dominate the results around the 90^{th} percentile. So, adding the sorption values from published literature led to a lower leaching endpoint (less leaching).

The correction procedure often leads to substantially lower values than the reported values. Figure 3-5 shows that in 7 out of the 28 batch values used for fitting the pH-dependent sorption, the corrected value was more than 50% of the reported value (the maximum was 67%). The absolute differences were more than 20 L/kg in 8 out of 28 cases. The absolute difference values tend to decline with pH while the relative differences tend to increase with pH (see Figure 3-6), as expected from the shape of the sorption curve. The relative difference at higher pH is more important for the endpoint of the calculation, i.e. the 90^{th}-percentile leaching concentration.

Table 3-2 Selected sorption values for fitting the pH-dependent sorption curve. Data with an unknown pH measurement method (assumed H_2O*) is given in italics.*

	soil	%OC	%OM	pH_{KCl}	pH_{CaCl2}	pH_{H2O}	K_D (l/kg)	K_F (l/kg)	K_{OC} (l/kg)	K_{OM} (l/kg)
Haberhauer	loam	2.40	4.14	4.30	4.60	5.17	1.39		57.98	33.63
Haberhauer	silt loam	2.70	4.65	7.96	7.90	8.41	0.78		28.81	16.71
Haberhauer	*clay loam*	*1.10*	*1.90*	*5.60*	*5.75*	*6.30*		*0.52*	*47.64*	*27.63*
Haberhauer	*clay loam*	*1.30*	*2.24*	*5.84*	*5.96*	*6.50*		*0.55*	*42.38*	*24.59*
Haberhauer	*clay loam*	*2.20*	*3.79*	*5.60*	*5.75*	*6.30*		*0.64*	*29.14*	*16.90*
Haberhauer	*clay loam*	*1.80*	*3.10*	*6.07*	*6.16*	*6.70*		*0.53*	*29.61*	*17.18*
Haberhauer	*clay loam*	*3.20*	*5.52*	*5.02*	*5.24*	*5.80*		*1.22*	*38.03*	*22.06*
Haberhauer	*clay loam*	*2.60*	*4.48*	*5.02*	*5.24*	*5.80*		*1.66*	*63.77*	*36.99*
Jensen	sand	1.80	3.10	4.91	5.14	5.70		0.71	39.44	22.88
Sorensen	sand	4.90	8.45	4.41	4.70	5.26	1.70		34.69	20.12
Sorensen	sandy loam	3.50	6.03	5.74	5.90	6.44	1.14		32.43	18.81
Fernando	*sand*	*0.52*	*0.90*	*4.09*	*4.43*	*5.00*		*0.67*	*128.59*	*74.59*
Fernando	*silt loam*	*1.22*	*2.10*	*5.02*	*5.24*	*5.80*		*0.78*	*64.28*	*37.29*
Goodwin	*loam*	*3.08*	*5.31*	*6.19*	*6.26*	*6.80*		*0.70*	*22.60*	*13.11*
Goodwin	*clay*	*1.26*	*2.17*	*6.42*	*6.47*	*7.00*		*0.22*	*17.66*	*10.25*
Montforts	*loam*	*0.64*	*1.10*	*6.07*	*6.16*	*6.70*		*0.19*	*29.38*	*17.09*
Montforts	*sandy loam*	*1.20*	*2.00*	*6.42*	*6.47*	*7.00*		*0.38*	*31.42*	*18.85*
Thorstensen	org.matter	37.70	64.99	2.41	2.90	3.50		146.20	387.80	224.94
Thorstensen	loam	2.50	4.31	5.30	5.50	6.05		1.25	50.00	29.00
Thorstensen	sandy loam	1.40	2.41	6.18	6.30	6.83		1.17	83.50	48.43
Vink	clay loam	2.80	4.83	7.70	7.59	8.10		0.67	23.96	13.90
Hiller	rendzina	4.59	7.91	6.34	6.39	6.93		0.65	14.24	8.26
Hiller	fluvisol	1.92	3.31	7.57	7.47	7.99		0.15	7.66	4.44
Hiller	pararendzina	2.49	4.29	7.42	7.34	7.86		0.24	9.58	5.56
Hiller	sandy loam	1.19	2.05	7.53	7.44	7.96		0.36	30.59	17.74
Hiller	silt loam	2.09	3.60	7.28	7.29	7.74		0.41	19.59	11.36
Hiller	silt loam	4.41	7.60	7.31	7.32	7.77		0.76	17.24	10.00
Hiller	silt loam	1.47	2.53	7.42	7.42	7.86		0.31	21.11	12.25
Haberhauer*	sandy loam	0.50	0.86	6.40	6.50	7.03	0.21	0.23	45.58	26.44

* column study

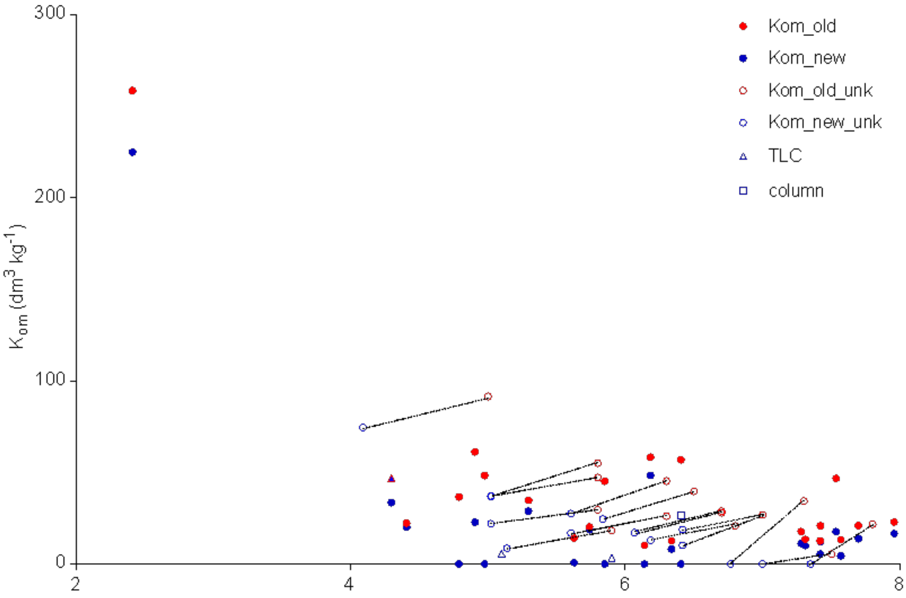


Figure 3-3 Reported (red symbols) and corrected (blue symbols) K_{OM} values remaining after selection step 4. The dotted lines connect original and corrected data points for which the pH measurement method was unknown.

Table 3-3 Results and statistics of the performed fits. A indicates fit without constraints, B indicates fit with delta-pH restricted to -0.2.

	A	B
Best-fit values		
$K_{OM,acid}$	243.9	238.6
$K_{OM,anion}$	17.34	16.72
RM	0.995	0.995
pK_a	3.73	3.73
pH shift	-0.2792	= -0.2000
Std. Error		
$K_{OM,acid}$	13.78	10.91
$K_{OM,anion}$	2.252	2.059
pK_a	0.1185	
pH shift		
$K_{OM,acid}$	215.6 to 272.3	216.2 to 261.0
$K_{OM,anion}$	12.71 to 21.97	12.49 to 20.94
pSH	-0.5227 to -0.03565	
Goodness of fit		
Degrees of freedom	26	27
R square	0.9351	0.9338
Absolute sum of squares	2950	3009
Sy.x	10.65	10.56
Constraints		
$K_{OM,acid}$	> 0.0	> 0.0
$K_{OM,anion}$	> 0.0	> 0.0
RM	= 0.9950	= 0.9950
pK_a	= 3.730	= 3.730
pH shift		= -0.2000
Points analysed	29	29

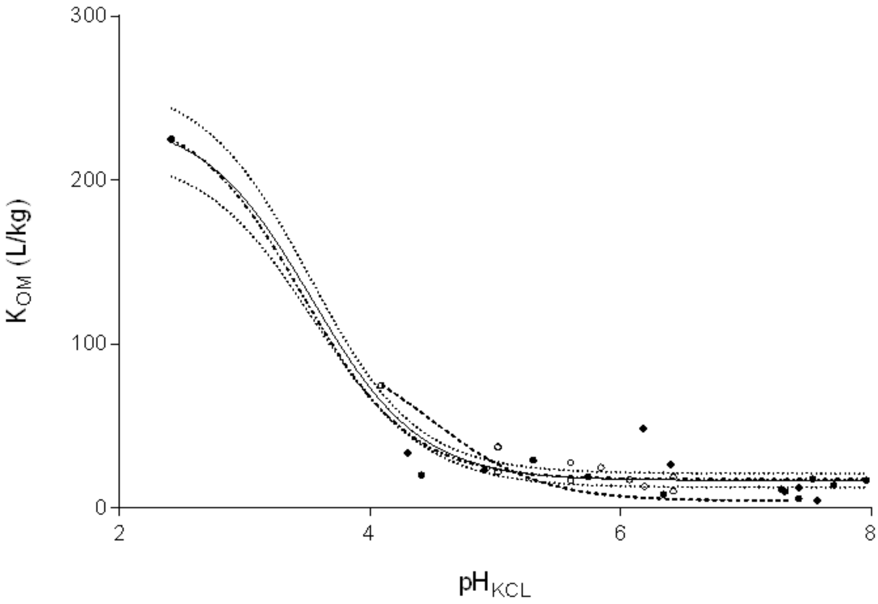


Figure 3-4 Fitted pH-dependent sorption curves for MCPA. Straight line: final fit with pH shift restricted to -0.2 (B in Table 3-3); dash-dotted line: unrestricted fit (A in Table 3-3); dotted lines: 95% confidence interval for the restricted fit; dashed line: fit on batch dossier values only. Circles indicate data with an unknown pH measurement method; dots indicate data with a known method. A few points are not visible due to overlap.

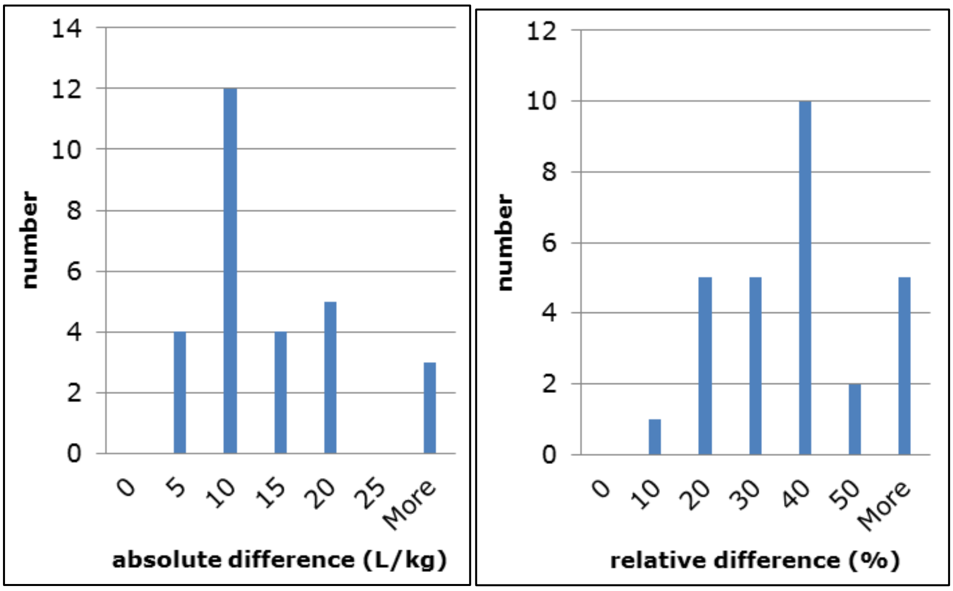


Figure 3-5 Histograms of the effect of correction procedure on individual sorption values. Left: absolute difference (L/kg) (corrected value is always lower); right: relative difference, i.e. 100(original-final)/original.*

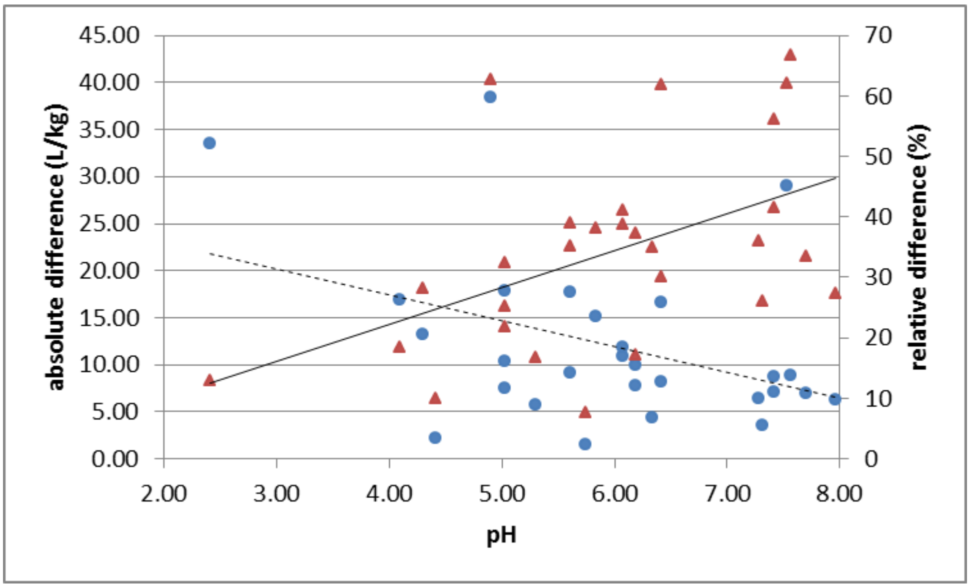


Figure 3-6 Relation between pH and effect of the correction procedure on individual sorption values. Left axis (blue dots): absolute difference (trend is downwards with increasing pH); right axis (red triangles): relative difference, i.e. 100(original-final)/original (trend is upwards with increasing pH).*

3.2.2 *Selection of the Freundlich exponent values*

For 38 out of the 115 batch experiments under consideration Freundlich exponent values were reported, including values that were calculated from the description.

As the value of the Freundlich exponent may have a pronounced effect on the calculated leaching, the reported exponent values need to be assessed critically and non-reliable values should be excluded when deriving the most appropriate value. The first criterion for selecting Freundlich exponent values is that the Freundlich coefficient is considered reliable. Therefore, only exponent values reported for experiments remaining after step 4 (see previous section) of the selection procedure for MCPA Freundlich sorption coefficients are considered here. Further selection criteria were:

- $\Phi > 0.8$
- Range in concentrations approximately two orders of magnitude or more
- At least three concentration levels
- PE > 0.1.

After applying these criteria, no Freundlich exponent values remained, i.e. there were no reliable exponent values associated with the selected Freundlich coefficients.

3.2.3 *Conclusions sorption*

After eliminating non-representative and unreliable sorption values, a total of 40 values remained, including 2 TLC values and 1 column value, on which the derivation of the function relating sorption of MCPA to the pH of the soil could be based. For 9 of these 40 values, the default correction procedure was judged overly conservative, based on comparison with other acceptable values. The two TLC values were also discarded, as higher sorption values from batch experiments were found for soils with approximately the same pH. So 29 values remained for the fitting procedure. The best fit results for the sorption equation were 239 ($K_{OM,acid}$) and 16.7 ($K_{OM,anion}$) L/kg, with the delta-pH value constrained to the lower boundary of -0.2. Using only batch sorption constants from the dossier, the results were 104 ($K_{OM,acid}$) and 4.2 ($K_{OM,anion}$) L/kg.

None of the experiments resulted in a reliable Freundlich exponent. Therefore, it is recommended to use the default value in calculations, i.e. 0.9.

3.3 Degradation

Table 3-4 gives a summary of the MCPA transformation experiments reported in the dossier. All these experiments were laboratory studies, and all were accepted for decision making. One other study was reported in the dossier but deselected because information on incubation conditions was lacking. All other experiments were judged sufficiently reliable. Experiments reported in the published literature were judged insufficiently reliable (see Appendix C). All accepted values were standardised with default procedures to the reference conditions for temperature (20 °C) and moisture (pF = 2), except the experiments evaluated by Vonk, which were already standardised. (http://www.rivm.nl/bibliotheek/rapporten/2015-0095MCPA_degradation_data.xlsm) It is possible that this standardisation was performed with an Arrhenius activation energy of 54 kJ/mol. All the values given in Table 3-4 are used in this report.

Table 3-4 Summary of MCPA transformation studies in the MCPA dossier (Ctgb 2003a).

Author	Soil type	pH_{KCl}	pH_{CaCl2}	pH_{H2O}	%OC	%OM	$DegT_{50}$ (d)
Matt	sandy loam	6.65	6.67	7.20	1.10	1.90	46.45
Matt	clay loam	7.35	7.28	7.80	1.04	1.80	64.87
Matt	clay loam	5.49	5.65	6.20	3.94	6.80	23.73
Matt	loam	7.12	7.08	7.60	1.39	2.40	21.23
Matt	loam	7.00	6.98	7.50	1.68	2.90	33.35
Matt		7.23	7.18	7.70	2.44	4.20	13.00
Matt	clay loam	5.26	5.45	6.00	6.79	11.70	11.54
Matt	sandy clay	7.12	7.08	7.60	2.32	4.00	11.48
Vonk							36.00
Vonk							29.00
Vonk							49.00
Montforts	sandy clay	3.63	4.02	4.60	10.32	17.80	65.91
Montforts	sandy loam	5.95	6.06	6.60	0.64	1.10	27.97
Montforts	loam	6.42	6.47	7.00	0.64	1.10	5.14
Montforts	sandy loam	6.07	6.16	6.70	1.16	2.00	8.08

pH method unknown for all experiments

The standard deviation of the natural logarithms of the $DegT_{50}$ values is 0.77, which is comparatively high and outside the range, 0.2–0.5, reported by EFSA (2012). The range reported by EFSA is to be expected for the degradation of substances in normal agricultural soils, where degradation is not dependent on soil properties and no adaptation of the

soil has taken place. A higher value indicates that further evaluation is appropriate.
If some of the soil were adapted to MCPA, a higher standard deviation is to be expected. Adaptation of soils to MCPA has been shown to occur (see for example Smith and Aubin (1991)). As far as possible, given the available information, adapted soils were excluded from the selection and thus adaptation is not expected to be the reason for the high standard deviation. A second reason for the high standard deviation could be differences in soil pH. Soil pH may influence both the availability of MCPA for degradation and soil micro-organisms responsible for the degradation. Although the $DegT_{50}$ value, pH=3.63, is higher than all other reported $DegT_{50}$ values, Figure 3-7 shows no obvious indication of a dependency of the degradation on soil pH, as the $DegT_{50}$ values are scattered. The slope of the regression line (not shown) is not significantly different from zero. However, no $DegT_{50}$ values in the pH range 3.65 – 5.25 are reported. Values in this range would be crucial to demonstrate dependency with pH as in this range the sorption changes dramatically. Also, there is no indication of a dependency on soil texture or soil organic matter content.

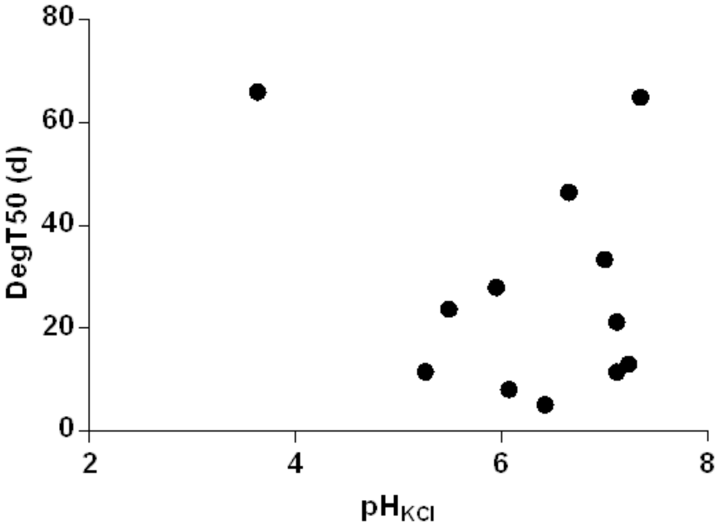


Figure 3-7 $DegT_{50}$ of MCPA in soil in relation to soil pH.

3.3.1 *Conclusions degradation*

No studies in the literature were found to be as reliable as information in the dossier. Considering all sufficiently reliable values (excluding doubles) and after conversion to reference conditions of pF=2 and T=20 °C, the geometric mean is 23.4 days. Furthermore, no clear relationship between degradation and soil properties (texture, pH, organic matter) was detected. Therefore, the geometric mean of 23.4 days is used in the assessment calculations.

3.4 **Selected usages and assessment**

This section assesses a few applications of MCPA in order to find out whether leaching was to be expected for applications according to label specifications about 25 years ago or is to be expected for applications according to current label specifications. For these assessments, $DegT_{50}$ and K_{OM} derived according to the methods developed in Boesten et al. (2015) (see Sections 3.2 and 3.3) were used.

MCPA was and is applied to many crops (including grass, cereals, potatoes and flower bulbs) as well as to (temporarily) uncropped soil and hard surfaces, but predominantly to grass. Spot applications to verges and dry ditches are also allowed. The selected usages are those in which MCPA is applied in the highest recommended dose and is not mixed with other herbicides. Usages with lower doses are expected to result in less leaching under otherwise comparable circumstances.

The typical late-season application to grass in the period 1980–1990 was assumed to be 1.2 kg/ha on 15 October (Asselbergs et al. 1996). An application in autumn is expected to lead to higher leaching concentrations than applications is spring and summer. This usage was therefore included in order to find out whether reported concentrations in deeper groundwater matched predictions based on late-season application.

In the current situation, only the period in which application of the substance is allowed has changed. This is now 1 March to 1 September. To cover the range of application dates, it was decided to perform simulations for applications on the first day of each month. The highest recommended dose for applications to crops is now 1.5 kg/ha (current situation), so somewhat higher than the historical application. The calculations for the current situation were also for grass.

The default parameter for interception by well-developed grass is 90%. The current approach is to subtract the amount intercepted from the application amount (FOCUS 2000), which implies that interception acts as a sink for the PPP. EFSA (2012) proposes accounting for dissipation of PPP from the leaf surfaces and using 100 m^{-1} for the wash-off factor in combination with a half-life of 10 d for other dissipation processes on the crop canopy, unless reliable measured values are available. The proposed wash-off parameter may lead to a substantial increase in the amount of PPP estimated to reach the soil surface. It was therefore decided to do simulations for both the currently used approach and the alternative proposed by EFSA, the latter being more conservative with regard to leaching.

The simulations were performed for both Tier 1 and Tier 2 of the decision tree for the usages indicated above. The physicochemical properties are given in Section 3.1 and the sorption and transformation data derived in Sections 3.2 and 3.3. Table 3-5 gives the calculated endpoints for seven application times and the two parameterisations. As prescribed in the authorisation procedure, the sorption parameter for MCPA used in the Tier 1 calculations is the $K_{OM,anion}$. All Tier 1 calculations, i.e. for the current and the alternative approach, led to endpoint concentrations above the threshold limit. Therefore, Tier 2 assessments had to be performed.

Leaching concentrations tend to become higher later in the application period, which can be attributed to the net precipitation becoming higher.

The chosen historical application at 15 October shows a somewhat lower leaching than the 1 September application. The difference can be largely attributed to the lower historical application rate (80% of the chosen current application rate).

Setting the parameters for wash-off and dissipation from leaves to the values recommended by EFSA (i.e. 100 m^{-1}) results in 90th-percentile concentrations that are a factor of 15–23 higher than those obtained using the FOCUS approach. Figure 3-8 shows the amounts of MCPA reaching the soil due to wash-off from the leaves, on one of the calculation plots. On average, 67% of the intercepted amount (i.e. approximately 1 kg/ha) is washed off and reaches the soil surface. The variability is caused by the timing of the rain event(s) shortly after application, giving more or less time to other dissipation processes, which were simulated with a DT_{50} of 10 days (default). So the amount reaching the soil surface directly or via wash-off is about seven times the amount estimated by the method assuming interception by leaves as a sink. The fact that the calculated leaching is more than seven times higher can be explained by the non-linearity of the sorption isotherm. Going from the default factor of 0.9 for the Freundlich exponent to a value of 1.0 (linear sorption) causes a factor of two difference in the calculated sorption at a concentration of 1 µg/L (Boesten et al. 2011, equation 25). This is further illustrated in Table 3-5. Assuming linear sorption, a difference of a factor of 6.8 is found between the cases with and without wash-off, whereas a difference of a factor of 21 was found for the equivalent situation with non-linear sorption (simulations with applications on 1 September).

Tier 2 simulations according to FOCUS (2000) all result in 90th-percentile leaching concentrations below the acceptability level of 0.1 µg/L, including that for application on 15 October. The highest concentration in the cumulative frequency distribution found for this parameterisation is slightly lower than 1 µg/L, for the application on 15 October. Simulations allowing for wash-off and appreciable dissipation from the leaf surfaces, as recommended by EFSA (2012) do not all lead to 90th-percentile concentrations below the acceptability level; only the applications in March, April and May do so. Better information on the wash-off and dissipation from leaves may lead to different conclusions. The highest concentration in the cumulative frequency distribution in the GeoPEARL simulation found for this parameterisation is slightly lower than 10 µg/L, for the application on 1 September.

Table 3-5 90th-percentile leaching concentrations (µg/L) for different calculation scenarios for MCPA.

Application	Canopy processes according to FOCUS (2000)		Canopy processes according to EFSA (2012)	
	Tier 1	Tier 2	Tier 1	Tier 2
Current, 1 Mar	0.42	0.0055	2. 7	0.092
Current, 1 Apr	0.41	0.0050	3.4	0.083
Current, 1 May	0.47	0.0050	5.2	0.083
Current, 1 Jun	0.47	0.0072	4.9	0.16
Current, 1 Jul	0.57	0.012	7.1	0.19
Current, 1 Aug	0.73	0.029	10	0.41
Current, 1 Sep	1.0	0.031	13	0.64
Current, 1 Sep#	2.40	0.31	20	2.1
Historical, 15 Oct	0.89	0.024	7.9	0.43

same run, but with linear sorption

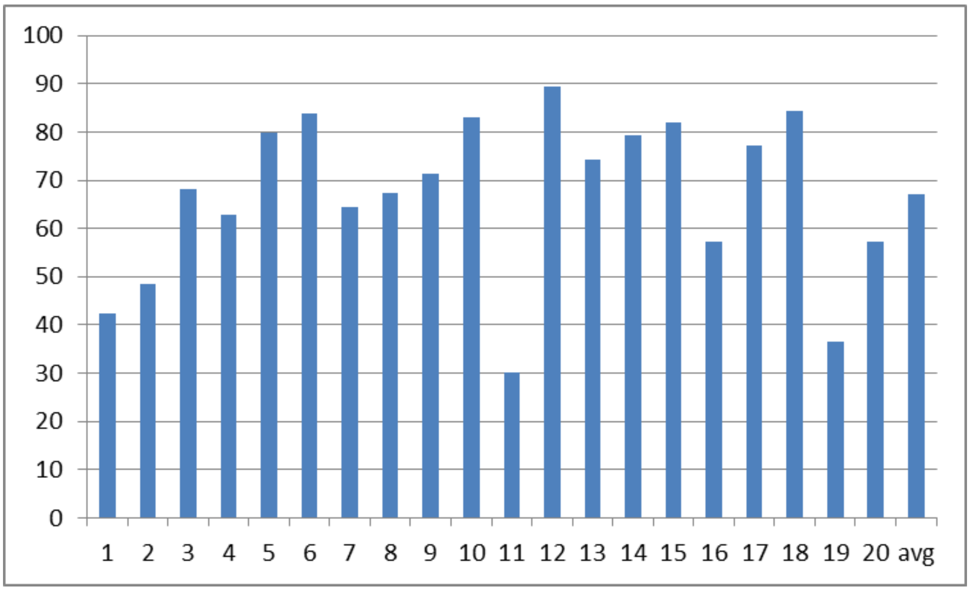


Figure 3-8 Amounts of MCPA (% of dose) reaching the soil via wash-off in one of the calculation plots in each of the simulation years.

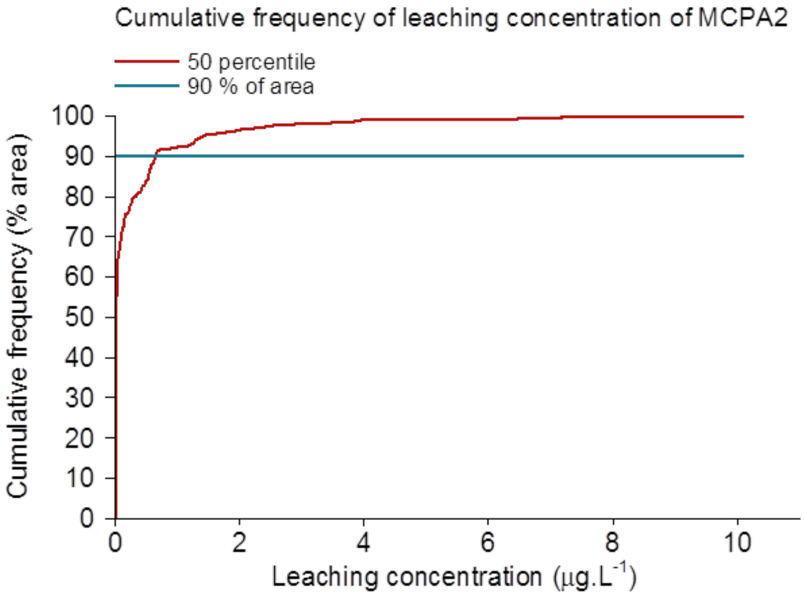


Figure 3-9 Potential leaching concentrations after MCPA application of 1.5 kg/ha on 1 September, with wash-off from leaves (the 2 in MCPA2 reflects the EFSA wash-off parameterisation).

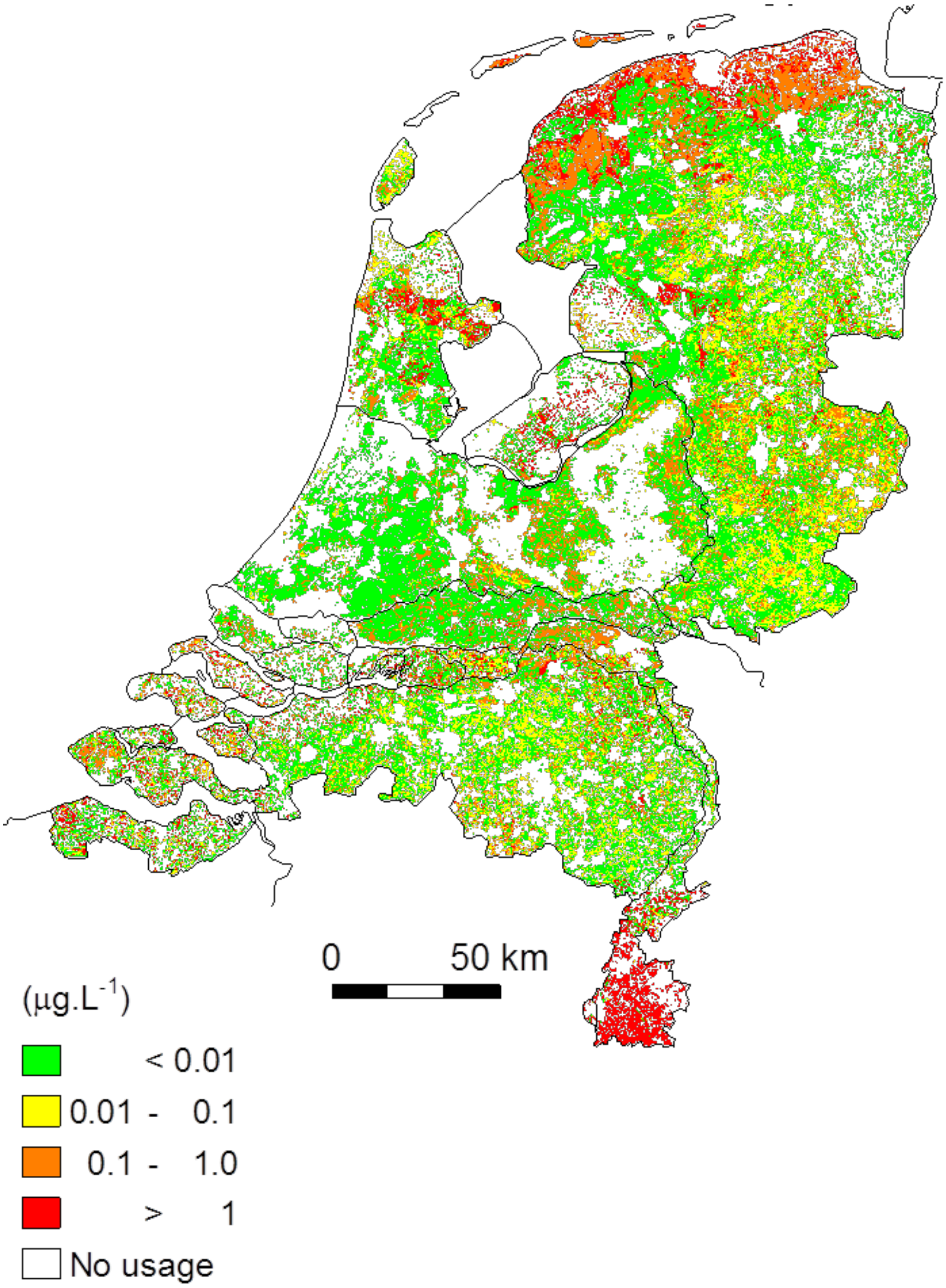


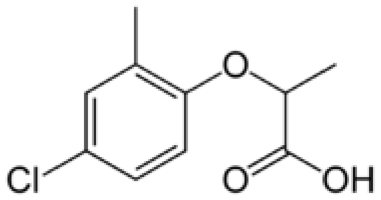
Figure 3-10 Map of MCPA leaching concentrations (50th percentiles) after application of 1.2 kg/ha on 1 September to grass, with wash-off from leaves.

4 Mecoprop

4.1 General information

The physicochemical properties of mecoprop-P needed for the simulation with PEARL are listed in Table 4-1.

Table 4-1 Physicochemical properties of mecoprop-P (Ctgb 2013).

Chemical name (IUPAC)	I-2-(4-chloro-o-tolyloxy)-propionic acid
Molecular formula	$C_{10}H_{11}ClO_3$
Structural formula	
Molar mass	214.65
Saturated vapour pressure	0.00023 Pa at 20 °C
Solubility in water	pH 3.1: 860 mg/L at 20 °C
Dissociation constant	pK_a = 3.86

4.2 Sorption

A total of 33 K_{OM} or K_{OC} values from laboratory batch studies are were found in the NL monograph and published literature. Of these, 11 K_{OC} values were not used because the soil organic matter content was below 0.5%. Of the remaining values, 13 were based on a concentration decrease in the study of less than 20%, which is not in accordance with OECD106. This was, however, not used as a deselection criterion, as the studies were performed before 2000. A detailed handling of the sorption data on mecoprop is given in the accompanying workbook on mecoprop. (http://www.rivm.nl/bibliotheek/rapporten/2015-0095mecoprop_sorption_data.xlsm) The pH was corrected according to the procedure described in section 3.6.2, i.e. Eqs (33a) and (34a), of Boesten et al. (2015). The K_{OM} was corrected according to the procedure given in Section 3.2 above. All measured Freundlich exponents were rejected because the ratio Φ in all studies was < 0.8 (see section 3.3.2 in Boesten et al. 2011).

Of the batch sorption studies referred to in this report, only a small number met the quality criteria. Therefore, TLC studies were also taken into account. The results of the TLC studies used are also summarised in the accompanying workbook. The R_{TLC} values of the Obrist studies 1–4 (Obrist 1986b) were determined from the graphs in the reports using the centre of mass to determine the movement of the substance. The K_{OM} values were calculated according to the procedure given in section 3.5 of Boesten et al. (2015). The K_F values were corrected for Freundlich adsorption using 1% of the mass applied to the plate. For the Obrist TLC studies, the applied mass was calculated assuming it was applied in a droplet of 0.05 ml.Note that the pH method used in the Obrist batch studies (b4–b7) (Obrist 1986a) and the Obrist TLC studies (t2–t5) was not reported. In accordance with Boesten et al. (2015), the H_2O measurement method for these studies was assumed, which is conservative.

All measurements of pH–K_{OM} from batch and TLC studies that were considered sufficiently reliable for further examination are shown in Table 4-2 and Figure 4-1.

Table 4-2 Mecoprop sorption data considered sufficiently reliable for further examination.

Author	Soil	%OC	%OM	pH_{KCl}	pH_{CaCl2}	pH_{H2O}	KD (l/kg)	K_F (l/kg)	Koc (l/kg)	K_{OM} (l/kg)
Matla	Sand	3.25	5.60	4.30	4.60	5.18	0.00	3.03	93.34	54.14
Matla	Sand	2.09	3.60	4.40	4.69	5.27	0.00	2.14	102.62	59.52
Matla	Sand	2.44	4.20	4.30	4.60	5.18	0.00	1.95	79.98	46.39
Obrist	Sand	0.46	0.80	4.79	5.04	5.60		0.00	0.00	0.00
Obrist	Sandy loam	1.33	2.30	7.12	7.08	7.60		0.00	0.00	0.00
Obrist	Silty clay loam	1.45	2.50	5.95	6.06	6.60		0.05	3.58	2.07
Obrist	Silt loam	3.42	5.90	6.19	6.26	6.80		0.28	8.33	4.83
Helweg	Sandy loam	1.39	2.40	6.30	6.36	6.90	0.00	0.00	0.00	0.00
Helweg	Sandy loam	1.51	2.60	6.07	6.16	6.70	0.00	0.00	0.00	0.00
Helweg	Sand	1.39	2.40	5.95	6.06	6.60	0.00	0.00	0.00	0.00
Haberhauer	Sandy	0.60	1.03	5.85	6.00	6.54		0.00	0.00	0.00
Haberhauer	Silt	2.40	4.14	4.30	4.60	5.17		0.75	31.29	18.15
Haberhauer	Sandy	0.50	0.86	6.40	6.50	7.03		0.06	11.60	6.73
Haberhauer	Calcareous	2.70	4.65	7.96	7.90	8.41		0.30	11.15	6.47
Rodriquez-Cruz	Sandy clay loam	1.67	2.88	6.07	6.16	6.70	0.30		18.06	10.48
Vink	Clay loam	1.62	2.80	7.70	7.59	8.10	0.67	0.87	53.39	30.97
Obrist	Sand	0.80	5.60	4.79	5.04	5.60	0.00	0.00	0.00	0.00
Obrist	Sandy loam	2.30	7.60	7.12	7.08	7.60	0.08	0.06	4.33	2.51
Obrist	Silt loam	2.10	7.00	6.42	6.47	7.00	0.08	0.05	4.20	2.44
Obrist	Silty clay loam	2.50	6.60	5.95	6.06	6.60	0.25	0.17	11.55	6.70
Obist	Sandy loam	2.30	7.60	7.12	7.08	7.60	0.05	0.03	2.56	1.48
Horvat	Sandy loam	1.70	5.10	5.10	5.33	5.87	0.25	0.31	31.34	18.18
Horvat	Loamy clay	5.80	5.90	5.90	6.05	6.56	0.41	0.52	15.50	8.99

References: Matla and Vonk (1993), Obrist (1986a), Helweg (1993), Obrist (1986b), Haberhauer et al. (2000), Vink and van der Zee (1997), Rodriguez-Cruz et al. (2006), Horvat et al. (2003)

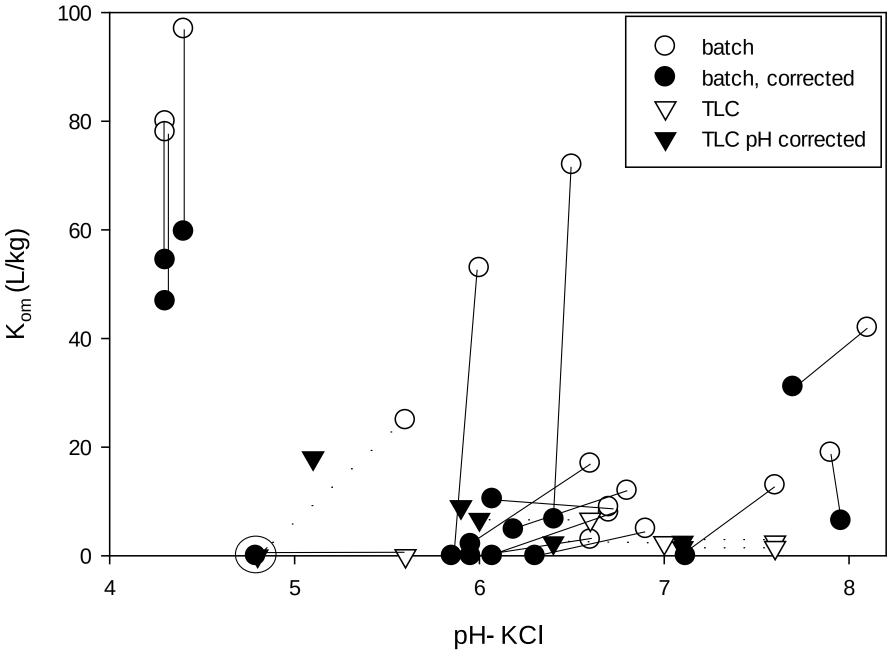


Figure 4-1 pH–K_{OM} data for mecoprop from batch and TLC studies. The large circle indicates that the batch and the TLC value in the circle are for the same soil. Dashed lines between markers are used where the pH method of the study was not known, and H_2O was assumed.

In the Horvat studies (t6, t7) (Horvat et al. 2003) R_F values were used, which generated lower sorption coefficients than central values. The TLC study was aimed to determine the impact of fertilizers on the movement of MCPA and mecoprop. The mobility of the pesticides was tested with deionized water and with different concentrations of salts, from 1% to 5% (w/v). The R_F determined for deionized water was used, being closest to the salt concentration of the soil solution. R_F values at 1% salt are approximately 0.60 (sandy loam) and 0.52 (loamy clay). The K_{OM} values calculated from the deionized water R_F values are probably somewhat overestimated.

The correction procedures applied in the workbook may result in overly conservative K_{OM} values. Therefore, corrections based on default assumptions on recovery were examined further in the light of all other values. Table 4-3 lists the K_{OM} values excluded from the fitting procedure, including the rationale for not including them.

The TLC studies with pH > 7 were all used because in this range no other K_{OM} values were available that overrule these values; although (i) the K_{OM} values are lower than the K_{OM} at pH 7.9, (ii) contact time in TLC studies is relatively short, and (iii) for the calculation an estimated theta is used.

The K_{OM} from batch study ID b-17 was not used because it is a lower limit value (see explanation in Boesten et al. 2015). Nevertheless, the K_{OM} values ID b-18 and ID b-19 were used for the fit because, although they are lower limit values, they are not outliers, and if the Freundlich exponent N is between 0.97 and 1, the K_{OM} values are close to the used value.

The 13 pH–K_{OM} pairs listed in Table 4-4 were used to fit the relation between pH and the sorption constant K_{OM} (see Figure 4-3). A $K_{OM,acid}$ of 79 L/kg and a $K_{OM,anion}$ of 3.8 L/kg were fitted, with pK_a 3.86 and a pH shift of 0.74 pH units. 3 gives the confidence interval of the fitted curve. The K_{OM} values used for fitting the pH-dependent sorption curve are given in Table 4-4.

Table 4-3 Combinations of K_{OM} and pH_{KCl} values for mecoprop not used.

Type of study	ID	pH_{KCl}	K_{OM} (L/kg)	Reason for excluding from fit
batch	b-17	4.30	18.15	This is a lower limit value; the concentration range in the study was 0.1 to 100 mg/L. A linear isotherm was assumed, hence high concentrations determine K_F value. Assuming N=0.9 would lead to a higher adsorption coefficient.
batch	b-4	4.79	0	The corrected K_{OM} value is zero, whilst within 0.3 pH units a K_{OM} value above zero is available.
batch	b-16	5.85	0	
batch	b-10	5.95	0	
batch	b-9	6.07	0	
batch	b-8	6.30	0	
batch	b-5	7.12	0	
TLC	t-1	7.10	0	Another TLC study has K_{OM} above zero, within 0.3 pH units of this value.
batch	b-33	7.70	31.11	K_{OM} is an outlier in this pH range. The Freundlich exponent of 0.58 is suspiciously low, whilst the fitting procedure is not reported (possibly not log-log fit).

Table 4-4 Selected combinations of K_{OM} and pH_{KCl} values for mecoprop.

Type of study	ID	pH_{KCl}	K_{OM} (L/kg)
batch	b-1	4.30	54.46
batch	b-3	4.30	46.90
batch	b-2	4.40	59.72
TLC*	t-6	5.10	18.00
TLC*	t-7	5.90	9.00
TLC	t-4	6.00	6.70
batch*	b-32	6.07	10.48
batch	b-7	6.19	4.83
TLC	t-3	6.40	2.40
batch*	b-18	6.40	6.73
TLC	t-2	7.10	2.50
TLC	t-5	7.10	1.50
batch*	b-19	7.96	6.47

* value taken from published literature

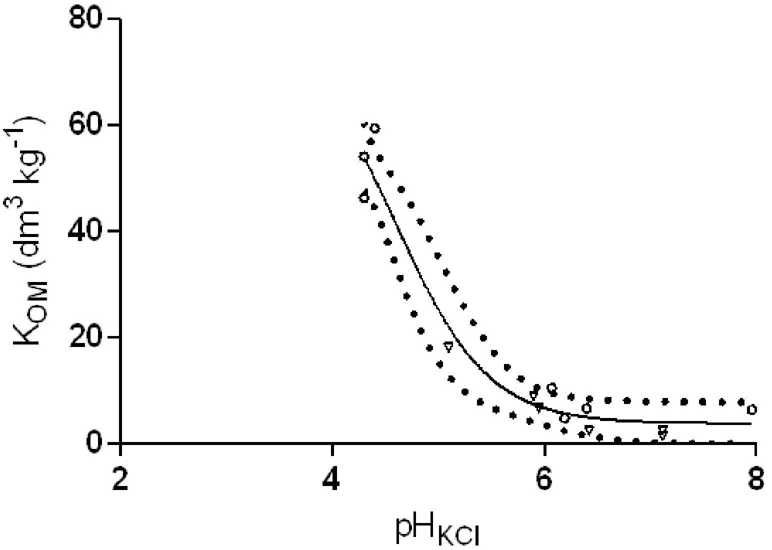


Figure 4-2 pH–K_{OM} fit curve on mecoprop data from batch studies and TLC studies with the 95% confidence interval. The triangles indicate TLC values, the circles batch values. All values are corrected according to the appropriate procedure.

To explore the impact of adding values from published literature on the obtained pH–K_{OM} relationship, the fit was repeated with the values of Table 4-2 excluding the K_{OM} values obtained from the literature. A $K_{OM,acid}$ of 62 L/kg and a $K_{OM,anion}$ of 0.2 L/kg were fitted, with pK_a 3.86 and a pH shift of 1.29 pH units. The resulting relationship is shown in Figure 4-4. With the addition of the published data, the sorption coefficients increase somewhat at higher pH and the confidence range is reduced. It is expected that, when using this curve for GeoPEARL calculations, the 90th-percentile concentration will be above the value when using the result of the fitting on all selected values. This assumption is based on the lower $K_{OM,anion}$ value, which will dominate the results around the 90th percentile. So, adding the sorption values from the literature leads to a lower leaching endpoint (less leaching). In this case it is mainly the K_{OM} at pH 5.1 that causes this effect.

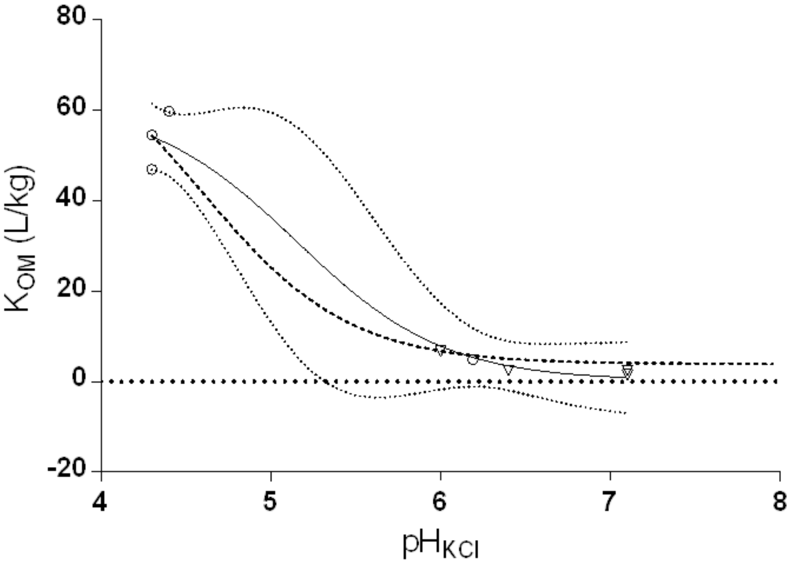


Figure 4-3 pH–K_{OM} fit curve without using published sorption data on mecoprop (solid line), with the 95% confidence interval of this curve (dotted lines). The triangles indicate the TLC values, the circles the batch values. The dashed line is the curve for all values (see also Figure 4-3).

4.3 Degradation

Laboratory degradation studies on half-lives in soil were reported in the NL monograph and in published literature. Details of the recalculation to half-lives under standard conditions and further processing of the data is given in the accompanying workbook (mecoprop_degradation.xlsm). After closer examination, no published study proved to be sufficiently reliable and all of them were rejected.

The measured $DegT_{50}$ values are normalised to pF2 (field capacity) by multiplying the measured $DegT_{50}$ value with a correction factor for the moisture content (Walker 1973). This correction factor, f_m, is calculated according to the equation $f_m = [\theta/\theta_{ref}]^{0.7}$. For the value of the reference moisture content (θ_{ref}) we used the water content at pF2 from different soil textures per table 5.2 of FOCUS (2000). Reported moisture content (θ) at 1/3 bar was 21% for silt loam, 15% for sandy loam and 25% for clay loam. The moisture content during the study was 80% of these values. The moisture content percentages for these soil types given in table 5.2 of FOCUS (2000) are 26%, 19% and 28%, respectively. Hence the resulting f_m values are 0.74 (silt loam), 0.72 (sandy loam) and 0.79 (clay loam). The soils studied by Romero et al. (2001) are calcareous soils amended with 10% of peat. Hence the study material was not a field soil, but manipulated. Therefore the study results were considered inappropriate for the current evaluation.

$DegT_{50}$ values were normalised to $DegT_{50}$ values at 20 °C using the Arrhenius equation with an Arrhenius activation energy of 65.4 kJ/mol (EFSA 2007).

Only the $DegT_{50}$ values of the List of Endpoints (8.2, 7.2, 7.0, 6.3 days at 20 °C), geometric mean 7.1 d Ctgb (2013), remained (see Table

4-5). From the data it is not possible to determine whether the transformation rate depends on the pH of the soil because the pH of the soils is not known.

Table 4-5 Evaluation of available transformation rates of mecoprop.

Author	Soil type	pH_{KCl}	pH_{CaCl2}	pH_{H2O}	%OC	%OM	$DegT_{50}$ (d)
LoEP	sandy loam						8.20
LoEP							7.20
LoEP							7.00
LoEP							6.30

4.4 Selected usages and assessment

Two usages were evaluated: (A) usage typical of the period 1980–1990 and (B) current usage.

Mecoprop is applied to many crops. The selected usages are those that were expected to generate the highest leaching. The usage typical of the period 1980–1990 was taken to be an application of 1.2 kg/ha to grass at 15 October (PD 1991).

The highest leaching of mecoprop can be expected from the highest dose. Current usage consists of the application of Duplosan to grass at a rate of 3 L/ha (i.e. mecoprop-P 1.8 kg/ha) (Ctgb 2013). The label prescribes application to eliminate stinging nettles when these have reached a height of 15–20 cm and are still growing. The permitted full-field application period is 1 March to 1 September, while spot application is allowed outside this period as well.

Leaching is calculated for full-field application of 1.2 kg/ha on 15 October, which represents the historical usage, and for full-field application of 1.8 kg/ha on 1 March and 1 September, which are considered to be representative of current usage. To cover the range of application timings, however, it was decided to perform simulations for applications on the first day of each month between March and September.

The default parameter for interception by well-developed grass is 90%. The fraction intercepted is subtracted from the applied amount (FOCUS 2000), which implies that the crop can be considered a sink for the PPP. EFSA (2012) proposes using 100 m^{-1} for wash-off from plant leaves and a half-life for dissipation on the crop canopy of 10 d. The proposed wash-off parameter may lead to a substantial increase in the amount of PPP estimated to reach the soil surface. It was therefore decided to do simulations according to the parameterisation proposed by EFSA as well.

The selected median $DegT_{50}$ value of 7.1 d has a weak basis, because only four $DegT_{50}$ values from the LoEP remained after applying the criteria for selection. Moreover, the quality of these four values could not be checked because the background information was not available and accessing the information was beyond the remit of the working group. It is, however, remarkable that the variation in the four values is so small, which may indicate a bias in the way these $DegT_{50}$ values were obtained.

In case the selected $DegT_{50}$ value was an underestimation, we did additional simulations with another $DegT_{50}$ value. We first assumed that the selected geometric mean of 7.1 d was based on $DegT_{50}$ values that were systematically too low, which would account for the fact that all four values were in the same lower part of the frequency distribution of $DegT_{50}$ values. We supposed that 7.1 d was one standard deviation below the geometric mean of the real distribution of $DegT_{50}$ values. To calculate the latter, we used the standard deviation (σ_g) of the natural logarithm of 0.47 based on eight data sets cited by EFSA (2010). The geometric mean of the real distribution could now be calculated as: $Ln(7.1) = Ln(\mu_g) - Ln(\sigma_g)$ and $Ln(\sigma_g) = 0.47$, hence $\mu_g = 11.4$ d. This is within the range of available degradation rates given in Table 4-5. Simulations for the current applications at 1 March and 1 September were therefore done with this $DegT_{50}$ of 11.4 d.

The simulations were performed for both Tier 1 and Tier 2 of the decision tree for the usages indicated above. The physicochemical properties are given in Section 4.1 and the derived sorption and transformation data in Sections 4.2 and 4.3. Furthermore, the Q10 value of 2.58 was used to account for the influence of temperature on the degradations (EFSA 2007). As prescribed, the selected sorption parameter for mecoprop in the Tier 1 calculations is the $K_{OM,anion}$. All Tier 1 calculations, for both the current and the alternative approaches, led to endpoint concentrations above the threshold limit. Therefore, Tier 2 assessments had to be performed. Table 4-6 gives the results of the calculations for the seven application times and two canopy parameterisations at both tiers. A graph showing the cumulative frequency diagram of the calculated potential leaching concentrations after mecoprop application of 1.2 kg/ha to grass is given in Figure 4-5, while a map of leaching concentrations after a 1.8 kg/ha spring application is given in Figure 4-6.

The chosen historical application results in a somewhat higher leaching concentration than the 1 September application, despite the lower application rate (2/3 of the chosen current application rate). This is due to the later timing of the historical application.

Setting the parameters for wash-off and dissipation from leaves to the value recommended by EFSA (i.e. 100 m^{-1} and 10 d, respectively) results in 90th-percentile concentrations that are a factor of 9–22 higher than those obtained using the FOCUS default parameters.

Simulations with the parameterisation according to FOCUS (2000) all result in 90th-percentile leaching concentrations below the acceptability level of 0.1 µg/L, including the result for the application on 15 October. The highest concentration for this parameterisation is 0.017 µg/L, for the application on 15 October.

Simulations allowing for wash-off and appreciable dissipation from the leaf surfaces, as recommended by EFSA (2012), lead to 90th-percentile concentrations above the acceptability level for the applications in August and September. The highest concentration found is 0.29 µg/L, for the application in September.

According to the current parameterisation of leaching processes, the acceptability limit of 0.1 µg/L is not exceeded. However, using the more conservative parameterisation proposed by EFSA, some exceedances of the limit of 0.1 µg/L of groundwater samples are to be expected. Note that the default EFSA parameterisation was used, which is worst case; a refined parameterisation would probably lead to lower concentrations.

The simulations with a $DegT_{50}$ of 11.4 d show that the leaching concentration increases by a factor of 15–18 (1 March) and 7–12 (1 September). For the 1 September application, the FOCUS approach leads to exceedance of the standard of 0.1 µ/L, as does the EFSA approach for the 1 March application. For the 1 September application the EFSA parametrisation exceeds the standard by a factor of 21. It can be concluded that the more realistic parameterisation of canopy processes represented by the EFSA approach, combined with the uncertainty in the geometric mean of the $DegT_{50}$, make encounters of mecoprop concentrations in groundwater above 0.1 µg/L likely.

Table 4-6 90th-percentile leaching concentrations (µg/L) for different calculation scenarios for mecoprop.

Application	$DegT_{50}$ (d)	Canopy processes according to FOCUS (2000)		Canopy processes according to EFSA (2012)	
		Tier 1	Tier 2	Tier 1	Tier 2
Current, 1 March	7.1	2.12	0.00080	2.39	0.0086
Current, 1 March	11.4	8.13	0.014	9.61	0.13
Current, 1 April	7.1	2.13	0.00016	2.54	0.0014
Current, 1 May	7.1	2.16	0.00026	3.06	0.0023
Current, 1 June	7.1	2.11	0.00033	2.57	0.0053
Current, 1 July	7.1	2.10	0.00050	2.66	0.0076
Current, 1 August	7.1	2.16	0.0025	3.22	0.056
Current, 1 September	7.1	2.25	0.013	6.81	0.29
Current, 1 September	11.4	8.71	0.15	24.4	2.1
Historical, 15 October	7.1	2.53	0.017	11.1	0.22

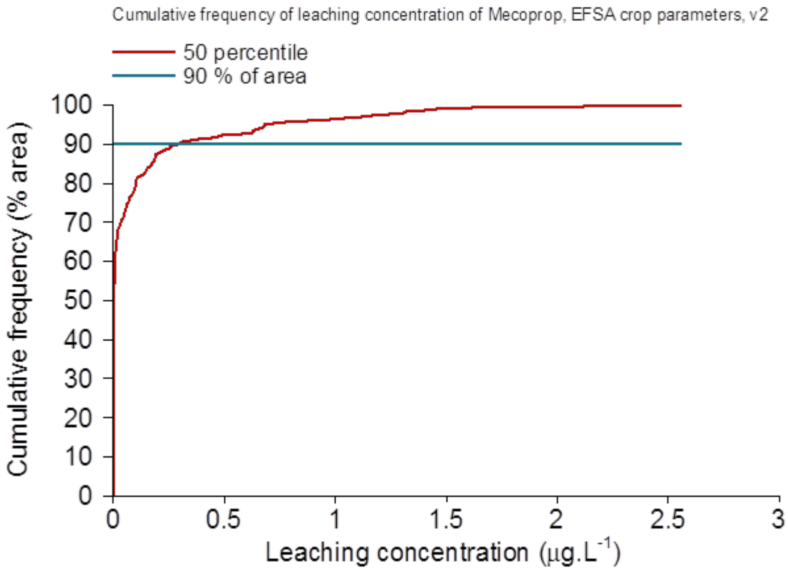


Figure 4-4 Potential leaching concentrations after mecoprop application of 1.8 kg/ha on 1 September, with wash-off from leaves (EFSA parameterisation of canopy processes).

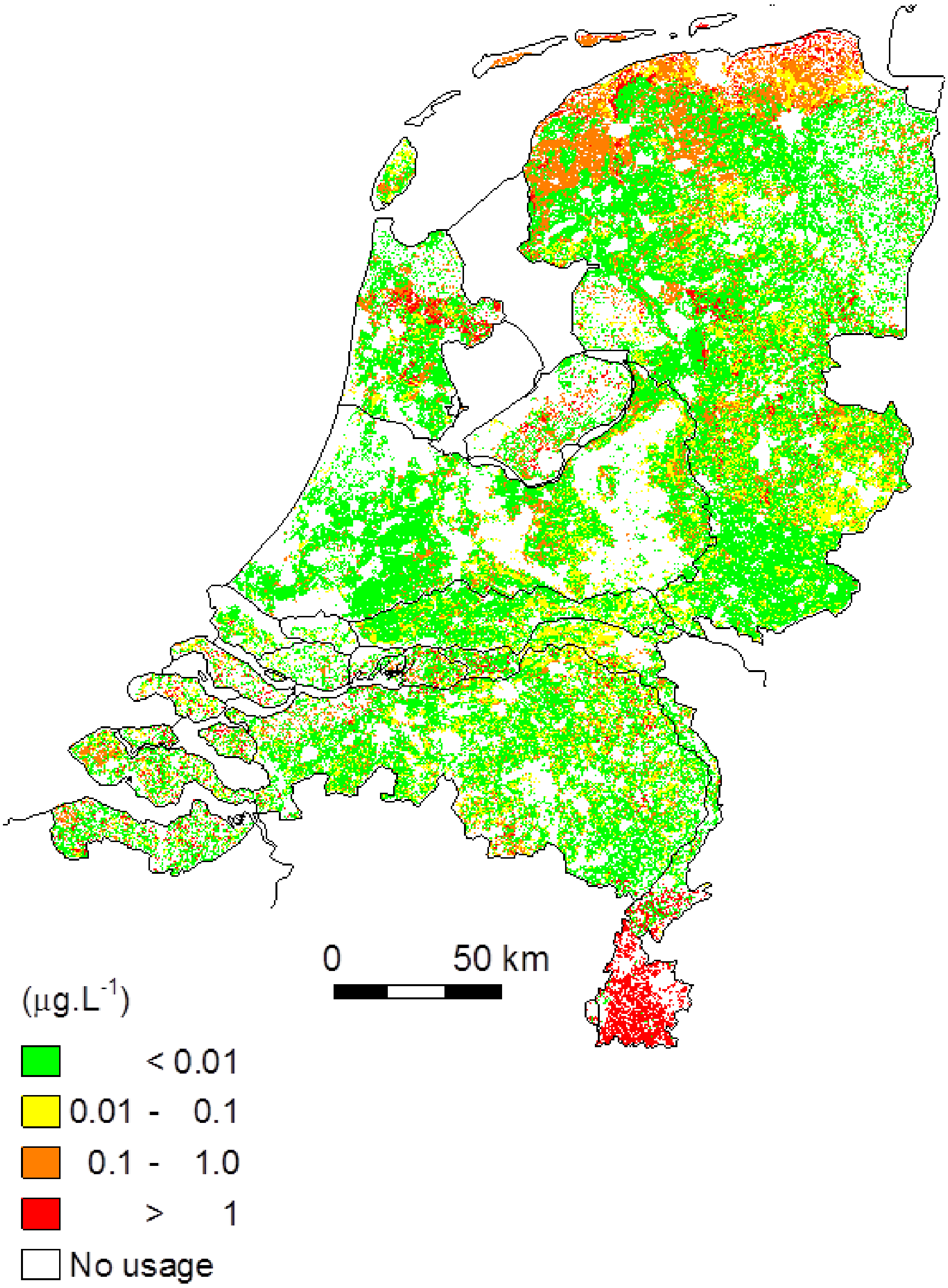


Figure 4-5 Map of mecoprop leaching concentrations (50th percentiles) after application of 1.8 kg/ha on 1 September to grass, with wash-off from leaves (EFSA canopy parameterisation).

5 Discussion, conclusions and recommendations

5.1 Bentazone

Our evaluation resulted in a DegT$_{50}$ endpoint of 16 d. The LoEP reports that DegT$_{50}$ values from seven laboratory studies at 20 °C ranged from 8 to 102 d (average of 45 d) and that DegT$_{50}$ values from four other laboratory studies at 20 °C ranged from 37 to 198 d (average of 90 d). The LoEP also reports that five German field studies showed a DegT$_{50}$ range of 4–21 d (average 14 d) and that two US field studies showed a DegT$_{50}$ of 6 d. So our 16 d is in the range of values reported by the field studies in the LoEP. However, it is not clear from the LoEP whether the reported field DegT$_{50}$ values have already been normalised.

Moreover, the LoEP does not give the endpoint of the DegT$_{50}$ to be used but sums up the results of the laboratory and field experiments. So we cannot compare our endpoint DegT$_{50}$ of 16 d with an endpoint in the LoEP.

The LoEP reports eight K$_{OC}$ values with their corresponding pH (without mentioning the pH method); we converted these to K$_{OM}$ values using the 1.724 factor (see Figure 5-1). These are the same eight sorption studies whose results were shown in Figures 2-1 A and B. Figure 2-1 showed that correcting for possible losses resulted in zero K$_{OM}$ values for all studies shown in Figure 5-1 except that with a K$_{OM}$ of about 100 L/kg. So the correction of the sorption for possible degradation during the study led to a very large difference between our K$_{OM}$ values and the K$_{OM}$ values in the LoEP. The endpoint K$_{OM}$ value(s) to be used for FOCUS scenario calculations are not given in the LoEP. So we cannot compare our K$_{OM}$–pH relationship with the endpoint in the LoEP.

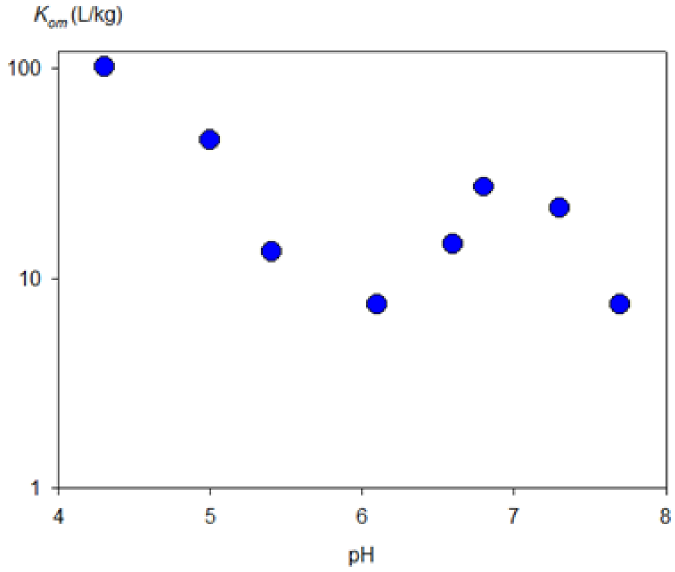


Figure 5-1 K$_{OM}$ of bentazone as a function of pH for the eight sorption studies reported in the LoEP.

The LoEP does not report any values for the Freundlich exponent. This probably indicates that the default value of 0.9 has been used (i.e. the same value as in our assessment).

The LoEP reports the results of three column leaching studies with three German standard soils. The percentages in the percolate ranged from 58% to 100% for soil 2.1, 61–100% for soil 2.2 and 56–100% for soil 2.3. These seem to be different studies from the studies with the BBA standard soil that we evaluated (see Table 2-2), although the results of the studies we evaluated are similar to the ones reported in the LoEP. Our Figure 2-3 indicates that percentages in the percolate close to 100% correspond to a linear sorption coefficient in the order of 0.01 L/kg or less, which will correspond to a K_{OM} in the range 0.1–1 L/kg. This is an order of magnitude lower than the lowest K_{OM}/K_{OC} values reported in the LoEP (see Figure 5-1), but the LoEP does not combine the results of the batch and the column studies.

The $DegT_{50}$ endpoint for bentazone was not influenced at all by data obtained from published literature. Four of the 13 K_{OM} values for bentazone were from the literature (the last three batch experiments listed in Table 2-4 plus the TLC study). After inspection of Figure 2-4, we concluded that omitting these four values would have resulted in approximately the same K_{OM}–pH relationship. So for the K_{OM} the value of adding published results was limited.

Using the sorption and degradation parameters derived in this report, bentazone failed to pass the second tier of the decision tree, for any of the application dates that were assumed. Calculated annual average concentrations are minimally a factor of 20 above the criterion value. For bentazone there are only slightly higher leaching concentrations when the more conservative EFSA parameterisation of canopy processes is used. This is primarily due to the relatively low interception values used, corresponding to the early growth stages of the crop. The additional amount of bentazone reaching the soil surface after wash-off is therefore small.

GeoPEARL simulations were done with two canopy parameterisations: the current FOCUS parameterisation, in which the loading mass intercepted by the crop does not wash off to the soil, and the parameterisation proposed by EFSA, where some of the intercepted mass washes off, the amount depending on the level of rainfall and the time between application and rainfall event. The GeoPEARL simulations for bentazone, which were done with a crop interception of 40%, showed that the difference in canopy parameterisation did not result in the differences in leaching concentrations that were expected. We question whether the way the crop is simulated in GeoPEARL, i.e. a hydrology simulation for only four types of land use, may lead to an underestimation of leaching concentrations. We recommend further checking the effects of land use and the canopy parameterisation in GeoPEARL.

The calculations were performed using the maximum prescribed application rates. For several crops, the prescribed application rates are lower than the maximum rates, but even using those rates would probably not reduce leaching concentrations to below the limit values. Additional information for second- or third-tier assessments would be necessary for a positive authorisation decision. The currently available data for third-tier assessment was not taken into account in this study.

5.2 MCPA

The leaching of MCPA has been evaluated at the EU level and the substance is included in the positive list, i.e. the list of substances that can be considered for authorisation at the national level in the EU (EC 2008). The physicochemical properties given in the dossier review report are identical to the values used in this report.

The half-lives of MCPA (at 20 °C, no information on moisture conditions) are reported to range from 7 to 41 days, whereas a value of 24 days (at 25 °C) was used to calculate PECsoil. Usable values were taken from the available values at Ctgb 15 (see Section 3.3). After correction for temperature and moisture conditions, these ranged from 5.1 to 66 days, with a geometric mean of 23.4 days. After correction to 20 °C and assuming optimum moisture conditions, the value used at the EU level is 37.6 days, which is greater than the geometric mean derived in this report. A scan of the literature did not reveal additional usable results on half-lives for MCPA.

K_{OC} values for MCPA in the EU document range from 10 to 157 L/kg (arithmetic mean 74 L/kg), based on experiments with eight soils originating from the USA. Conversion to K_{OM} leads to a range of 5.2-91 L/kg, with an arithmetic mean of 43 L/kg. The range of K_{OM} values used for deriving endpoints in this report is 4.4–225 L/kg; 29 values were found to be sufficiently reliable. This means that slightly lower as well as much higher values were found.

Based on the information in the dossier summary, it is likely that four out of the eight values from the EU dossier are present in the final selection in this report, as the final selection contains four soils originating from the USA. If so, the minimum and maximum value found in this report are outside the range of soil pH covered by the EU dossier values. The maximum is found at much lower pH, whereas the minimum is found at higher pH. For all four soils, the correction procedures led to lower sorption values. Corrected values were approximately 20–60% lower than reported values, at between 7 and 18 L/kg.

The EU document states that sorption of MCPA is dependent on soil pH, but that this is likely to be significant only at pH below 4. The analyses in this report show that soil pH is likely to have significant effects below pH_{KCl} values of 5.5 (pH_{H2O} values below 6.2), which means that pH-dependent effects may be expected in agricultural soils. In a conservative assessment, it would not be appropriate to use results from soils with pH_{KCl} values below 5.5 in the calculation of the geometrical mean. Two of the US soils in the selection have pH values below that value.

Freundlich exponents for the eight soils in the EU dossier range from 0.5 to 0.72. The average value of these exponents would rank rather low in the distribution of exponent values reported in the literature. Moreover, the values were judged not sufficiently reliable to be used for risk assessments.

Our view was that the sorption experiments needed re-interpretation, as standard OECD106 interpretation attributes non-recovered substance to sorption (see Boesten et al. 2011, 2015, and Section 3 of this report). Re-interpretation led to different endpoints and, in particular, lower sorption constants.

Sorption values from the literature proved useful for the further characterisation of the sorption of MCPA. The quality of a number of the experiments results in the literature was equal to or better than the quality of the values in the dossier. Including values from the literature led to higher K_{OM} values at higher pH, leading to a lower leaching estimate for risk assessment.

If an assessment of leaching potential were conducted using the standard FOCUS parameterisation of wash-off and other dissipation processes and the newly derived parameters on sorption and transformation, MCPA would not pass the first tier of the decision tree. Calculations for all application times resulted in a leaching concentration above the threshold value when the $K_{OM,anion}$ was used for the sorption. According to second-tier calculations, MCPA could be authorised, as calculated 90^{th}-percentile leaching concentrations are below the threshold level of 0.1 µg/L for all uses on grass (other uses were not investigated, see Table 3-5).

The decision would be quite different if the parameterisation for dissipation processes as recommended by EFSA were applied. As expected, a first-tier calculation for the Kremsmünster scenario leads to a leaching concentration above 0.1 µg/L. In the second tier, some of the label applications would lead to 90-percentile leaching concentrations above the value of 0.1 µg/L (Table 3-5). Wash-off from plant leaves leads to additional loading of the soil and 90^{th}-percentile leaching concentrations exceed the threshold limit with applications after 1 June. Mitigation would be needed if the authorisation were to be renewed.

According to the Dutch Environmental Indicator database on uses of PPP on crops (Kruijne et al. 2011), more than 50% of the total use of MCPA is on grassland, grass seed cultivations and grass strips in orchards. Some of these applications are made late in the growing season. Other major applications are to wheat and barley, in early spring. As simulations indicate that higher leaching concentrations are to be expected later in the season, it is conservative to relate concentrations in groundwater on the late-season application to grassland.

5.3 Mecoprop

Mecoprop is on the list of active ingredients authorised in the EU. The $DegT_{50}$ used for the evaluation in the present report is derived from the four values given in the List of Endpoints (European Commission 2003). For the sorption coefficient, the LoEP gives: mecoprop K_{OC} 20–43 L/kg in four different soils (pH 5.6–7.6); mecoprop-P K_{OC} 135–167 L/kg in three sandy soils (pH 4.3–4.4). It is indicated that mecoprop-P is a weak acid and thus the adsorption is expected to be higher the lower the pH is. There are no data from column studies. For soil TLC, RF values for mecoprop are 0.74–1.0. Three lysimeter studies (spring application to summer wheat of 1.2 kg/ha on acidic sandy loam and of 2.24 kg/ha on sandy soil, both in Germany, and autumn application to winter wheat of 2.0 kg/ha on sandy soil in Denmark) gave leaching concentrations < 0.03 µg/L, of 0.13–0.18 µg/L, and of 77 and 0.16 µg/L, respectively. Hence it is indicated that adsorption of mecoprop depends on the pH of the soil, which is supported by the data. The lowest K_{OC}, of 20 L/kg, i.e. a K_{OM} of 12 L/kg, is four times the $K_{OM,anion}$ used in this report. This higher K_{OM} from the LoEP is probably due to not correcting the sorption coefficient for losses in the experiment. Hence even when the pH dependence of adsorption of mecoprop is taken into account, and the lowest values (determined with high-pH soils) are used in the risk assessment, the leaching of mecoprop to groundwater is underestimated in the current EU assessment, because the sorption coefficient is overestimated.

For mecoprop the derived $DegT_{50}$ of 7.1 days has a weak basis. None of the transformation studies in the dossier or the studies found in scientific literature could be used to derive the $DegT_{50}$ because they did not meet the criteria set for determining the transformation rate (Boesten et al. 2015). For this validation we had to revert to four values from the LoEP for mecoprop (European Commission 2003), for which minimal data is found in the dossier. The variation in the four values was small; hence some bias is suspected. To revert to the studies was beyond the remit of the workgroup. To compensate for the weak basis of the $DegT_{50}$ of mecoprop, some additional GeoPEARL calculations were done with a higher $DegT_{50}$ of 11.4 days.

For a crop from which maximal leaching is expected, using the current guidance for GeoPEARL calculations, with the derived $DegT_{50}$ of 7.1 days and the sorption - pH relation, the leaching of mecoprop to groundwater was below the limit of 0.1 µg/L. A value of between 0.01 and 0.1 µg/L was found for the application in September, which, in contrast to the current authorisation, would lead to a restriction in the use of mecoprop in protection zones around drinking water wells. Repeating the calculations, but using a $DegT_{50}$ for mecoprop of 11.4 days results in leaching concentrations between 0.01 and 0.1 µg/L in March and above 0.1 µg/L in September. Hence, additional restrictions on the use of mecoprop would be indicated. Considering the weak basis of the derived $DegT_{50}$ of 7.1 d, this would likely be the result if additional transformation studies were carried out. For future evaluations of mecoprop we therefore recommend additional transformation studies.

Upcoming guidance from EFSA regarding crop processes was also applied to the GeoPEARL calculations. This resulted in leaching concentrations above 0.1 µg/L for late summer application (September), regardless of the weak basis of the derived $DegT_{50}$ value. Hence using the improved guidance from Boesten et al. (2015) in combination with upcoming guidance for crop parameterisation in leaching models would result in restrictions on the use of mecoprop that are not required with the current approach and substance parameters.

Published literature data for $DegT_{50}$ values was not selected because its quality was considered to be insufficient.

Five of the 13 values selected to determine the pH–K_{OM} relationship were from the literature. The effect of including the published K_{OM} values on the determination of the pH–K_{OM} relationship was that the average K_{OM} value increased somewhat at higher pH and the confidence range decreased. A single value measured at a low pH (5.1), in a range where no other values were available, was the main cause of this effect. Hence published values are relevant to the determination of the pH–K_{OM} relationship, when few dossier values are available. Using the pH–K_{OM} relationship determined from published values for GeoPEARL calculations will result in lower values for the leaching of mecoprop to groundwater.

5.4 Overall conclusions

Including data from published literature had no influence on the $DegT_{50}$ endpoint for all three substances.

Including data from published literature had a negligible influence on the K_{OM}–pH relationship for bentazone (admittedly, the literature consisted of only three K_{OM} values, measured by the RIVM and Alterra for three Dutch soils). In contrast, the inclusion of published values had considerable influence for MCPA and some effect on results for mecoprop. Adding data from the literature led to an increase in the K_{OM} in the most important part of the K_{OM}–pH curve and it is therefore expected to decrease the estimated leaching concentration of MCPA and mecoprop.

The proposed correction procedure for the K_{OM} (Eqn 18 in Boesten et al. 2015) had a very large effect on the K_{OM}–pH relationship for all three substances: (i) for bentazone, for nine of the ten batch studies a correction of more than 50% was calculated; (ii) for MCPA, 7 of the 28 batch studies had a correction of 50% or more and another 10 of the 28 had a correction between 40 and 50% (Figure 3-5); (iii) for mecoprop, 13 of the 20 batch studies had a correction of more than 50%. As mentioned before, OECD106 requires there to be a decrease of at least 20% in concentration for the indirect method to be used, so a large part of the sorption studies were not acceptable according to the OECD106 guideline (which prescribes the direct method in such cases). The background to this is that OECD106 was published in 2000, whereas most of the above-mentioned studies were conducted before 2000.

The proposed correction procedure for pH (to use pH_{H2O} if the pH measurement method is not reported – i.e. a conservative approach) had a considerable effect on the K_{OM}–pH relationship for two of the substances: (i) for bentazone, the pH of eight of the ten batch studies was corrected; (ii) for MCPA, the pH of 12 of the 28 batch studies was corrected. For mecoprop, the effect was more limited: the pH of five of the 23 K_{OM} values (Table 4-2) was corrected. The correction led in these cases to a decrease in the pH of about 0.5–1.

The proposed quality check for the Freundlich exponent N had a very large effect: none of the measured N values was considered acceptable.

For all three substances the application to grass at 1 September (current use) and at 15 October (historical use) was identified as the most relevant one. It is remarkable that the application to grass in the autumn was identified as the likely cause of the monitoring findings for all three substances are weak acids with pH-dependent sorption.

Our simulations for mecoprop and MCPA (applications on a well-developed grass cover) showed that use of the default parameters for wash-off and degradation on plant surfaces as recommended by EFSA (2012) may lead to a considerable increase in leaching as compared to the current approach (i.e. treating interception by the crop such that leaf surfaces act as a sink for the PPP, in accordance with FOCUS 2009).

Our GeoPEARL simulations for bentazone showed that GeoPEARL is not suitable for simulating wash-off from plant surfaces. Because it is hydrologically based on only three crops (maize, potatoes and grass), GeoPEARL does not simulate the wash-off realistically.

Using the three example substances, bentazone, MCPA and mecoprop, to test the guidance proposed by Boesten et al. (2011) resulted in the following improvements to that guidance (see Boesten et al. 2015, for details):

- The guidance for the assessment of the total mass of substance remaining in the soil profile in field persistence studies was greatly simplified, the 2011 guidance being overly complicated.
- The guidance for soil column leaching studies and soil TLC studies was extended, the 2011 guidance not being sufficiently detailed.
- The guidance for the assessment of the K_{OM}–pH relationship was improved by modifying a considerable number of minor items.

Our experiences indicate that following the guidance proposed by Boesten et al. (2011) will lead to a considerable increase in the estimated leaching concentrations of substances with low sorption coefficients (i.e. the substances that are likely to be most critical for the leaching assessment). A more detailed assessment of the impact on the registration of pesticides, which was impossible within the time constraints of this project, may be necessary.

5.5 Recommendations for further research

The current version of GeoPEARL cannot simulate realistically the wash-off from plant surfaces as recommended by EFSA (2012). Therefore, we recommend improving the simulation of wash-off from plant surfaces in GeoPEARL.

The quality criteria for the Freundlich exponent (which led to rejection of all reported values of this exponent) have a weak scientific basis. We therefore recommend underpinning or improving these criteria through an analysis of the error in this exponent.

As described above, the default correction factor of 10% degradation/loss used for the indirect batch studies led to a very large decrease in K_{OM} values. Many of the corrected K_{OM} values were subsequently discarded because they appeared too conservative in the light of other evidence (i.e. other batch studies or soil column or TLC studies). This 10% is a conservative value based on the requirement in OECD106 to achieve at least 90% recovery of the test substance. It now seems that this 10% is somewhat too conservative. We therefore recommend a literature review on the relationship between the degradation rate in batch systems and the degradation rate in soil or water sediment studies, which is likely to permit a less conservative approach.

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Appendix A Glossary

BBCH	Code for the growth stage of a crop
c_{st}	Standardised concentration
Ctgb	Board for the authorisation of plant protection products and biocides (College voor de toelating van gewasbeschermingsmiddelen en biociden)
$DegT_{50}$	Half-life of a substance in soil (d)
DT_{50}	Half-life for dissipation (d) – in this report dissipation from leaves
DFOP	Double first order in parallel transformation (degradation) kinetics
EFSA	European Food Safety Authority
EZ	Ministry of Economic Affairs (Ministerie van Economische Zaken)
FOCUS	Forum for the coordination of pesticide models and their use
HS	Hockey Stick transformation (degradation) kinetics
IenM	Ministry of Infrastructure and the Environment (Ministerie van Infrastructure en Milieu)
IUPAC	International Union of Pure and Applied Chemistry
K	sorption coefficient
K_F	Freundlich sorption coefficient
K_{OC}	Soil organic carbon normalised sorption constant (L/kg)
K_{OM}	Soil organic matter normalised sorption constant (L/kg)
LOD	Limit of detection
LoEP	List of Endpoints in an assessment report
LOQ	Limit of quantification
LSC	Liquid scintillation counting
OECD	Organisation for Economic Co-operation and Development
OECD106	OECD guideline 106 (OECD 2000)
PEARL	Pesticide emission at regional and local scales
PEC	Predicted Environmental Concentration
PPP	Plant protection product
Q10	Factor describing the influence of temperature on transformation reactions
R_{TLC}	Retardation factor based on centre of mass
R_F	Retardation factor based on movement of the front
RIVM	National Institute for Public Health and the environment (Rijksinstituut voor Volksgezondheid en Milieu)
SFO	Single first order transformation (degradation) kinetics
TLC	Soil thin layer chromatography

Appendix B Details of MCPA studies

Table B-1 Summary of MCPA transformation studies from published literature sources.

Author	Soil type	pH	OM %	Storage conditions	Incubation conditions	DegT$_{50}$ (d)	DegT$_{50}$ (corr.)	Remarks
Laboratory studies								
Buser and Müller (1997)	sandy loam	7	2.8	air-dried to 22%, then part to 2%, then kept in clay pot for a few days	20–23 °C, daylight, 25% water	6.9	7.8[#]	temperature and duration of storage not given; single bulk sampled repeatedly; DegT$_{50}$ calculated via log-transformation
Müller and Buser (1997)	sandy loam	7	1.6	air-dried, then kept in clay pot for a few days	20–23 °C, daylight, 18% water	9.2	10.4[#]	temperature during storage not given for first 30 d
Lindahl et al. (2005)						3.5		exposed soil; no further information
Smith and Aubin (1991)	clay	7.25	2.5	used immediately	85% of FC at 20 °C in the dark	<8 d		no measurements at t=0; only 3 data points; transformation faster in exposed soils
Vink and van der Zee (1997)	clayey calcareous fluvisoil	8.1[b]	4.8	fresh, undisturbed samples used immediately	18 °C	3.9		water content not stated; substance brought on top of micro columns, not mixed through soil
Field studies								
Crespin et al. (2001)	loam	8.08[b]	0.9	n/a	with irrigation, application rate ca 100 mg/kg	5.1		not normalised, leaching occurred, too high application rate
Non-relevant studies								
Suzuki et al. (2001)	sandy loam/ sandy clay loam	6.8/6.5	8.4/5.5	two weeks at 25 °C	mixture top/subsoil open and sealed; 23% water	9		inadequate sampling regime (0,25,30,60 d,..)
Harrison et al. (1998)	aquifer							rapid breakdown under aerobic conditions

pH a $CaCl_2$, b H_2O, unknown otherwise

\# corrected for an average incubation temperature of 21.5, not corrected for water content, which is equivalent to pF2 or higher.

Table B-2 Summary of MCPA transformation studies from dossier.

Author	Soil type	pH	OM %	Storage conditions	Incubation conditions	$DegT_{50}$ d	$DegT_{50}$ d (corr.)	Remarks
Matt	sandy loam				EPA 162-1	24	24	
review	sandy loam	7	2		23 °C, 13% FC	~8		no further info
	sandy loam	7.2	1.9		26 °C, 100% FC	32	51.4	
	clay loam	7.8	1.8		26 °C, 100% FC	41	65.8	
	clay loam	6.2	6.8		26 °C, 100% FC	15	24.1	
	loam	7.6	2.4		26 °C, 100% FC	14	22.5	
	loam	7.5	2.9		26 °C, 100% FC	22	35.3	
		7.7	4.2		20 °C, 85% FC	13	11.6	
	clay loam	6.0	11.7		20 °C, 85% FC	14	12.5	
	sandy loam	7.6	4		20 °C, 85% FC	14	12.5	
Vonk						36	36	
						29	29	
						49	49	
Montforts	sandy clay	4.6	17.8	pF 5–6		69	69	
	sandy loam	6.6	1.1	pF 5–6		32	32	
	sandy loam	7.6	4			3	3	=review
	clay loam	6	11.7			7	7	=review
	clay	7.7	4.2			9	9	=review
	loam	7	1.1			8	8	
	sandy loam	6.7	2			12	12	

Table B-3 Overview of MCPA sorption studies.

ID	Author	Year	Soil texture	pH	Method	K_{OM}	Selection
b1	Haberhauer	2000	sand	6	$CaCl_2$	45.2	
b2	Haberhauer	2000	loam	4.6	$CaCl_2$	46.9	
b3	Haberhauer	2000	loamy sand	6.5	$CaCl_2$	56.9	
b4	Haberhauer	2000	silt loam	7.9	$CaCl_2$	23.0	
b5	Haberhauer	2001	clay loam	6.3	NR	45.3	
b6	Haberhauer	2001	clay loam	6.5	NR	39.7	
b7	Haberhauer	2001	clay loam	6.3	NR	26.1	
b8	Haberhauer	2001	clay loam	6.7	NR	28.0	
b9	Haberhauer	2001	clay loam	5.8	NR	29.5	
b10	Haberhauer	2001	clay loam	5.8	NR	47.3	
b11	Jensen	2004	sand	5.7	H_2O	61.2	
b12	Jensen	2004	sand	5.7	H_2O		step 1
b13	Sorensen	2006	sand	4.7	$CaCl_2$	22.4	
b14	Sorensen	2006	sand	4.8	$CaCl_2$	42.5	step 3
b15	Sorensen	2006	sand	5.3	$CaCl_2$	42.1	step 3
b16	Sorensen	2006	sand	5.5	$CaCl_2$	17.4	step 3
b17	Sorensen	2006	sand	5.6	$CaCl_2$	8.7	step 3
b18	Sorensen	2006	sand	4.9	$CaCl_2$	11.6	step 3
b19	Sorensen	2006	sand	4.5	$CaCl_2$	104.4	step 3
b20	Sorensen	2006	sand	4.3	$CaCl_2$	127.6	step 3
b21	Sorensen	2006	sandy loam	5.9	$CaCl_2$	20.4	
b22	Sorensen	2006	sandy loam	6	$CaCl_2$	19.3	step 3
b23	Sorensen	2006	sandy clay loam	7.9	$CaCl_2$	1.3	step 3
b24	Sorensen	2006	sandy loam	8.1	$CaCl_2$	1.0	step 3
b25	Sorensen	2006	sandy clay loam	8	$CaCl_2$	8.0	step 3
b26	Sorensen	2006	sandy clay loam	7.8	$CaCl_2$	16.6	step 3
b27	Fernando	1992	clay loam	7.8	NR	21.8	
b28	Fernando	1992	sand	5	NR	91.5	
b29	Fernando	1992	silt loam	5.8	NR	55.2	
b30	Fernando	1992	sandy loam	7.3	NR	34.4	
b31	Goodwin	1988	silt loam	5.9	NR	18.4	
b32	Goodwin	1988	loam	6.8	NR	20.9	
b33	Goodwin	1988	sandy loam	7.5	NR	5.5	step 4
b34	Goodwin	1988	clay	7	NR	26.9	
b35	Montforts	1997	loam	6.7	NR	29.0	
b36	Montforts	1997	sandy loam	7	NR	27.0	
b37	Thorstensen	2001	org. matter	2.9	$CaCl_2$	258.5	
b38	Thorstensen	2001	loam	5.5	$CaCl_2$	34.8	
b39	Thorstensen	2001	sandy loam	6.3	$CaCl_2$	58.4	
b40	Aamand	2004	sandy loam	6.76	$CaCl_2$	59.6	step 1
b41	Aamand	2004	sandy loam	6.46	$CaCl_2$		step 1
b42	Aamand	2004	sandy loam	6.28	$CaCl_2$	61.4	step 1
b43	Aamand	2004	loamy sand	7.16	$CaCl_2$		step 1
b44	Aamand	2004	sand	5.24	$CaCl_2$	303.8	step 1
b45	Aamand	2004	sand	6.08	$CaCl_2$		step 1
b46	Hiller	2006	subsoil	8.2	H_2O	14.3	step 3
b47	Shang	1998	sandy loam (NT)	4.8	$CaCl_2$	36.5	step 1

ID	Author	Year	Soil texture	pH	Method	K_{OM}	Selection
b48	Shang	1998	sandy loam (CT)	5.59	$CaCl_2$	23.2	step 1
b49	Shang	1998	clay (NT)	4.68	$CaCl_2$	97.4	step 1
b50	Shang	1998	clay (CT)	5.02	$CaCl_2$	105.6	step 1
b51	Vink	1997	clay loam	8.1	H_2O	20.9	
b52	Vink	1997	silt loam	8.8	H_2O	17.4	step 3
b53	Hiller	2006	rendzina	6.93	H_2O	12.7	
b54	Hiller	2006	fluvisol	7.99	H_2O	13.3	
b55	Hiller	2006	cambisol	6.76	H_2O	10.2	
b56	Hiller	2006	pararendzina	7.86	H_2O	12.7	
b57	Hiller	2006	luvisol	6.32	H_2O	14.1	
b58	Hiller	2009	sandy loam	7.96	H_2O	53.4	step 1
b59	Hiller	2009	sand	5.76	H_2O	43.5	step 1
b60	Hiller	2010	sandy loam	7.96	H_2O	46.8	
b61	Hiller	2010	sand	5.76	H_2O	48.3	
b62	Socias-Viciana	1999	sandy loam	7.6	H_2O	77.3	step 4
b63	Hiller	2012	silt loam	7.28	KCl	17.8	
b64	Hiller	2012	silt loam	7.31	KCl	13.5	
b65	Hiller	2012	silt loam	7.42	KCl	20.9	
b66	Hiller	2012	silt loam	7.55	KCl	18.4	step 3
b67	Hiller	2012	silt loam	7.67	KCl	37.0	step 3
b68	Hiller	2012	loam	7.53	KCl	12.3	step 3
b69	Hiller	2012	silt loam	7.55	KCl	31.3	step 3
b70	Jacobsen	2008	sand	4.9	$CaCl_2$	77.9	step 2
b71	Jacobsen	2008	sand	5.3	$CaCl_2$	63.8	step 2
b72	Jacobsen	2008	sand	5.8	$CaCl_2$	81.1	step 2
b73	Jacobsen	2008	sand	6.3	$CaCl_2$	72.8	step 2
b74	Jacobsen	2008	sand	4.2	$CaCl_2$	131.1	step 2
b75	Jacobsen	2008	sand	5.2	$CaCl_2$	54.4	step 2
b76	Jacobsen	2008	sand	5.1	$CaCl_2$		step 1
b77	Jacobsen	2008	sand	5.6	$CaCl_2$	27.1	step 2
b78	Jacobsen	2008	sand	4.9	$CaCl_2$	81.5	step 2
b79	Jacobsen	2008	sand	4.7	$CaCl_2$	76.9	step 2
b80	Jacobsen	2008	sand	4.5	$CaCl_2$	89.1	step 2
b81	Jacobsen	2008	sand	4.1	$CaCl_2$	187.5	step 2
b82	Jacobsen	2008	sand	5.2	$CaCl_2$	59.6	step 2
b83	Jacobsen	2008	sand	4.6	$CaCl_2$	98.2	step 2
b84	Jacobsen	2008	sand	5.5	$CaCl_2$	47.1	step 2
b85	Jacobsen	2008	sand	5.3	$CaCl_2$	67.7	step 2
b86	Jacobsen	2008	sand	4.8	$CaCl_2$		step 1
b87	Jacobsen	2008	sand	6	$CaCl_2$	245.9	step 2
b88	Jacobsen	2008	sand	5.3	$CaCl_2$	72.5	step 2
b89	Jacobsen	2008	sand				step 1
b90	Jacobsen	2008	sand	4.6	$CaCl_2$	94.7	step 2
b91	Jacobsen	2008	sand	5.3	$CaCl_2$	33.4	step 2
b92	Jacobsen	2008	sand	4.2	$CaCl_2$	166.1	step 2
b93	Jacobsen	2008	sand	5	$CaCl_2$	126.2	step 2
b94	Jacobsen	2008	sand	5	$CaCl_2$	126.2	step 2
b95	Jacobsen	2008	sand	4.6	$CaCl_2$	112.9	step 2

ID	Author	Year	Soil texture	pH	Method	K_{OM}	Selection
b96	Jacobsen	2008	sand	4.7	$CaCl_2$	166.8	step 2
b97	Jacobsen	2008	sand	4.8	$CaCl_2$	85.3	step 2
b98	Jacobsen	2008	sand	4.6	$CaCl_2$	56.6	step 2
b99	Jacobsen	2008	sand	5.8	$CaCl_2$	18.9	step 2
b100	Jacobsen	2008	sand	5.2	$CaCl_2$	69.6	step 2
b101	Jacobsen	2008	sand	4.7	$CaCl_2$	87.0	step 2
b102	Jacobsen	2008	sand	5.6	$CaCl_2$		step 2
b103	Jacobsen	2008	sand	5.1	$CaCl_2$		step 1
b104	Jacobsen	2008	sand	4.3	$CaCl_2$		step 1
b105	Jacobsen	2008	sand	4.8	$CaCl_2$	81.2	step 2
b106	Jacobsen	2008	sand	5.3	$CaCl_2$	46.4	step 2
b107	Jacobsen	2008	sand	4.3	$CaCl_2$	94.7	step 2
b108	Jacobsen	2008	sand	5.4	$CaCl_2$	81.2	step 2
b109	Jacobsen	2008	sand	4.9	$CaCl_2$	110.2	step 2
b110	Jacobsen	2008	sand	4.5	$CaCl_2$	84.1	step 2
b111	Jacobsen	2008	sand	4.7	$CaCl_2$	87.0	step 2
b112	Jacobsen	2008	sand	4.7	$CaCl_2$	116.0	step 2
b113	Jacobsen	2008	sand	4.6	$CaCl_2$	110.2	step 2
b114	Jacobsen	2008	sand	5.1	$CaCl_2$		step 2
b115	Riise	1994	silty clay loam	5.6	H_2O	36.6	
c1	Haberhauer	2002	sandy loam	6.5	$CaCl_2$	26.4	
c2	Haberhauer	2002	silt loam				step 1
c3	Celis	2007	sandy clay loam	8.5	H_2O		step 1
c4	Hiller	2010	sandy loam	7.96	H_2O		step 1
c5	Hiller	2010	sand	5.76	H_2O		step 1
c6	Socias-Viciana	1999	sandy loam	7.6	H_2O		step 1
c7	Montforts	1997	sand				step 1
c8	Montforts	1997	loamy sand				step 1
c9	Montforts	1997	sandy loam				step 1
c10	Montforts	1997	sand				step 1
c11	Montforts	1997	loamy sand				step 1
c12	Montforts	1997	sandy loam				step 1
c13	Montforts	1997	loam	7	NR	21.3	step 1
c14	Montforts	1997	sandy loam	6.7	NR	38.8	step 1
t1	Montforts	1997	silty clay loam			1.7	step 1
t2	Montforts	1997	sandy loam			0.0	step 1
t3	Montforts	1997	silt loam			3.8	step 1
t4	Horvat	2003	sandy loam	5.1	KCl	5.6	
t5	Horvat	2003	clay loam	5.9	KCl	3.4	

In the ID column: b batch study, c column study, t TLC study. The Selection column gives the selection step at which the record was deleted from further consideration.

References: Haberhauer et al. (2000); Haberhauer et al. (2001); Jensen et al. (2004); Sorensen et al. (2006); Fernando (1992); Goodwin and Laskowski (1998); Montforts and Verdam (1997); Thorstensen et al. (2001); Aamand et al. (2004); Hiller et al. (2006); Shang and Arshad (1998); Vink and van der Zee (1997); Hiller et al. (2009); Hiller et al. (2010); Socias-Viciana et al. (1999); Hiller et al. (2012); Jacobsen (2008); Haberhauer et al. (2002); Celis et al. (2007); Horvat et al. (2003). Riise et al. (1994).

Details on the handling of selected column leaching and soil TLC studies.

Column studies
Haberhauer et al. (2002) performed a column leaching study with ^{14}C-labelled MCPA, using columns 49 mm in diameter and with a net length of 30 cm. The columns were packed such that the dry bulk density was 1.41 kg/L (report states 1.34). The eluate, 0.02 molar $CaCl_2$ solution, was applied in two portions of 200 mm each on consecutive days (at a rate of 1 ml per minute). The leachate was collected in fractions of 100 ml. After leaching, the columns were sliced into 6 cm segments and extracted.

TLC of the extracts did not show any transformation products. No transformation products were found in the leachate either. Overall MCPA recovery was approximately 90%. Approximately 80% of the applied radioactivity was in the leachate, peaking in the third fraction (no further information).

The penetration depth of 30 cm was reached with the third fraction of eluate. A conservative estimate is therefore that the penetration depth was reached with 200 ml of eluate. According to the formula (equation 22 in Boesten et al. 2011):

$$KD = \frac{(W - \theta Z)}{\rho Z}$$

a sorption below zero is calculated. Approximately 250 ml would be necessary to displace 1 pore volume. The calculated sorption is 0 L/kg, without correction.

Hiller et al. (2010) performed a column leaching study with two soils. 50 ml leaching solution was brought on top of 15 cm columns on 15 consecutive days. The leaching peak occurred after 1 pore volume percolated through the soil. This gives a calculated sorption of 0 L/kg.

TLC studies
For TLC studies K_D is calculated from equation 28 in Boesten et al. (2011) with the retardation factor R_F defined as the movement of the substance divided by the movement of the waterfront. For TLC studies θ is taken as 0.3 and ρ is taken as 1. In the study by Horvat et al. (2003), the R_F was measured according to the frontal method; the values had to be read from a graph. As further information was lacking, it was assumed that c_{st} was 1 mg/L, which is generally conservative in soil TLC studies.

Appendix C References concerning MCPA considered not useful/relevant for this evaluation

Aamand et al. (2004)

Remarks

Report contains mineralisation values, not DegT$_{50}$ values.

No relevant data.

Brown et al. (2000)

Remarks

Lysimeter study without original information on sorption and transformation.

No original study on DegT$_{50}$ of MCPA.

Buser and Müller (1997)

Description

Soil taken from garden location where MCPA had never been used. After sampling, soil was air-dried at room temperature to 22% moisture content, then sieved (10 and 4 mm). A part was then further dried to approximately 2%. Then the soil was kept in a clay pot for a few days until the start of the incubation study.

Soil:

	pH	OM	Water content
		%	%
Sandy loam	7	1.6	25

Addition: 1.25 mg/kg.

Incubation: single bulk, 25% water content, 20–23 °C, daylight

Sampling: single samples, 10 gram (wet weight) until day 45

Analysis: extraction with methanol, quantification with HRGC/MS/MS

DegT$_{50}$ regression of ln(c/c0) assuming first order kinetics

Results

DegT$_{50}$	MCPA
Period 0–30 days	9.2
Period 30–45 days	2.6

Remarks

Storage conditions between sampling and incubation studies were not reported.

No acclimatisation before incubation.

Authors refer to Müller and Buser, using the same soil.

Recovery not given.

Water contents recalculated.

Raw data not available.

Calculation of half-lives using ln transformation.

Arbitrary selection of the breakpoint time.

Data considered to be not sufficiently reliable for this evaluation.

Crespin et al. (2001)

Description

2,4-D and MCPA were applied to the top 10 cm of an agricultural sandy clay loam soil ((47% clay, 20% silt, 33% sand), pH$_{H2O}$ 8.08, OM 0.9%). The initial MCPA content in the 10 cm layer was 78 mg/kg, approximately an order of magnitude higher than contents resulting from agricultural applications. Temperatures were recorded (both air and soil), but only range, average minimum and average maximum are given. Precipitation was recorded to be 10 mm over 50 days. Six irrigations of 17 mm each were supplied. 12 samples were taken over a 50-day period. Sampling depth was down to 40 cm, sliced into four layers of 10 cm.

Results

MCPA and 2,4-D dissipated from the top 10 cm following first-order kinetics with a half-life of 5.1 and 4.9 days, respectively. MCPA and 2,4-D were detected in the second and third layers shortly after the first irrigation and in the fourth layer shortly after the second irrigation. Chlorophenol metabolites were detected in the top layer.

Remarks

Calculated half-lives refer to dissipation.

It is not possible to derive standardised half-lives as daily (soil) temperatures, and water content of the soil layers is not given.

MCPA contents for the four layers are given graphically only.

The initial MCPA content is considered to be too high.

Fogg et al. (2003)

Remarks

Not a soil study.

Fredslund et al. (2008)

Remarks

Paper contains mineralisation values, not $DegT_{50}$ values.

No relevant data.

Harrison et al. (1998)

Description

In situ in aquifer and laboratory studies with aquifer materials with the PPP MCPA, dichlorprop and mecoprop, at various redox conditions.

Results

Rapid breakdown was observed under active aerobic conditions, while no degradation occurred under active anaerobic conditions. Under aerobic conditions, degradation occurred from 2000 µg/l down to 10 µg/L in a few weeks. No information on kinetics, no half-lives reported.

Remarks

The results are considered not relevant for agricultural soils.

Jensen et al. (2004)

Description

Table 1. Selected properties of the soil material from Fladerne Bæk

		silt and clay (%)	sand (%)	gravel (%)	pHwater	org. Ctot (%)	Ntot (%)	SAd (m^2/g)	CEC cmol (+)/ 100 g)
topsoil	(A)	4.8	94.7	0.5	5.7	1.8	0.12	0.29	16.2
subsoil	(C)	0.6	98.8	0.6	5.7	0.1	0.03	0.83	6.2

Sorption isotherms were obtained in batch experiments where triplicate samples of 1.0 g of each soil-sorbent mixture were treated with 10 mL of 0.01 M CaCl2 solution with initial concentrations (Ci) of MCPA of 0.1, 1.0, or 10 mg/L and activities of 330–360 Bq/mL. NaN_3 (0.01% w/v) was added to the suspensions to inhibit microbial activity. Temperature 10 °C. Based on OECD.

Results

Sorption:

Soil/sorbent	pH	K_F	nF	r^2
AN	5.25	1.9 (0.1)	0.89 (0.04)	0.988
CN	5.30	< 0.3		

K_{OM} 61.2 L/kg

Transformation:

Mineralisation based on CO_2 evolution

Remarks

Values not usable to derive $DegT_{50}$.

Juhler et al. (2008)

Description

Study on the variability of dissipation of pesticides from soil. Study included 62 samples (topsoils and subsoils) in which MCPA dissipation was studied. 55 samples had a half-life shorter than 2 years (average 9.5 days), 7 had a half-life longer than 2 years.

Remarks

Paper does not state individual sample descriptions, nor result values.

Lindahl et al. (2005)

Description

Main part of the paper deals with modelling. Paper states that transformation experiments were performed and that kinetics were not first order. Nevertheless a first-order transformation rate was used for the modelling. Individual data not given. In parameter overview, the transformation rate was stated to be 0.198 ($DegT_{50}$ 3.5 days).

Remarks

No original study on $DegT_{50}$ of MCPA; value not used.

Lindhardt et al. (2000)

Description

Report contains degradation data for MCPA (and other PPP) included in the dossier 1997. It is, however, unclear how the different data relate to each other. Average DT_{50} data of the Smith (1982) study, the soils with ID 10–12, are 13.45, 12.75, 13.8 days. Soils were each incubated with MCPA or MCPA in combination with other PPP (20 experiments each).

Remarks

Results showed very little variation.

Müller and Buser (1997)

Description

Soil taken from garden location where MCPA had never been used. After sampling soil was air dried at room temperature to 22% moisture content, then sieved 10 and 4 mm. Then the soil was kept in a clay pot for a few days, until the start of the incubation study.

Soil:

	pH	OM	Water content
		%	%
Sandy loam	7	1.6	25

Addition: 1.25 mg/kg (MCPA in a mixture of MCPA, mecoprop, 2,4-D, dicamba, dichlorprop at 1.25 mg/kg each; separate experiments with racemic and enantiopure mecoprop and dichlorprop)

Incubation: 25% water content, 20–23 °C, daylight

Sampling: 10 g single portion at several points in time over 35 days

Analysis: extraction with methanol, quantification with HRGC/MS

$DegT_{50}$ regression of ln(c/c0) assuming first-order kinetics

Results

$DegT_{50}$	MCPA	Remark
Period 0–16 days	7.3	With racemic mixtures mecoprop and dichlorprop
Period 16–35 days	3.1	With racemic mixtures mecoprop and dichlorprop
Period 0–14 days	5.0	With R-enantiomers mecoprop and dichlorprop
Period 0–14 days	6.1	With S-enantiomers mecoprop and dichlorprop

Remarks

Temperature at which soil was kept between sampling and incubation not mentioned.

Water content recalculated.

Total initial herbicide concentration in soil is somewhat high (6.25 mg/kg).

Recovery not given.

Incubation not in the dark.

One single jar incubated; mixing of soil at each analysis time.

Raw data not available.

Arbitrary choice of breakpoint time.

Data considered not sufficiently reliable for this evaluation.

Rasmussen et al. (2005)

Description

Transformation studied by measuring CO_2 evolution.

Remarks

Mineralisation values cannot be used as basis for $DegT_{50}$.

Roulier and Jarvis (2003)

Remarks

Modelling study; no original $DegT_{50}$ value.

Smith and Aubin (1991)

Description

Soil:

Type	pH	Sand	Silt	Clay	OM
		%	%	%	%
clay	7.25	25	25	51	2.5

After sampling, soils were immediately pre-incubated in the dark at 20 °C.

Addition: 50 g moist soil at 85% of field capacity, 2 mg/kg MCPA

Incubation: at 20 °C in the dark

Sampling: 4, 8, 16 days after application

Analysis: extraction with acetonitrile, water and glacial acetic acid (80:20:2.5 v/v/v)

Quantification LSC

Recovery >90%

Results

In control soil (not treated earlier with 2,4-D or MCPA) 63±8%, 40±6% and 14±8% MCPA was recovered after 4, 8 and 16 d, respectively. In a second experiment, with the same set-up, 57±7%, 40±2% and 10±2% was found. The degradation was stated to follow first-order kinetics. Enhanced degradation was found in soil from a plot treated annually

with MCPA for a period of 37 years. Remarks Check on first-order kinetics at only three time points. Half-lives not reported; calculation method not given. All extracted radioactivity was attributed to parent substance, based on an earlier observation (using a TLC technique) that all activity could be attributed to the parent. Data considered to be not reliable enough for the current evaluation.
Sorensen et al. (2006) Description Soils: A) Fladerne Baek, pH_{CaCl2} 4.7, OC 4.9%, <20 µm 4.6%, >20 µm 95.4% (topsoil) B) Avedore pH_{CaCl2} 5.9, OC 3.5%, <20 µm 33.4%, >20 µm 66.6% (non-agricultural topsoil) Sorption: Soil/water ratio 1:1 (for MCPA), single concentration (not given) 3 replicates, NaN_3 to prevent transformation, 10 °C 96h *Results* Not all data given. From graph: Kd A) 1.89 l/kg, B) 1.23 l/kg; K_{OM} A) 21.3 l/kg B) 20.7 l/kg. Transformation: Mineralisation was studied Remarks Mineralisation values cannot be used as basis for $DegT_{50}$.
Vink and van der Zee (1997) Description Methods: MCPA, mecoprop, aldicarb and simazine. Soil (35.2/49.1/15.7), pH_{H2O} 8.1, OC 2.8%; sediment (22.6/43.8/33.6), pH_{H2O} 8.8, OC 1.6% Sorption experiment: soil/water ratio 0.4, sediment/water ratio 0.3 Contact time in total 26 h (6 hours shaking). Temperature 5 °C Incubation (aerobic): temperature 18 °C, C0 4.5 mg/kg applied with a syringe on top of undisturbed soil columns. Mecoprop 7, MCPA 5 measurement data. (Maximum incubation time 200 days for anaerobic incubations) Results Mecoprop: K_{OM} 42.3 l/kg (soil) 1/n = 0.58, 22 l/kg (sediment) 1/n = 1.01. $DegT_{50}$ 4 d (aerobic), 41 d (low oxic), > 693 d (anaerobic). MCPA: K_{OM} 20.9 l/kg (soil) 1/n = 0.83, 17.4 l/kg (sediment) 1/n = 1.07. $DegT_{50}$ 3.6 d (aerobic), 38.2 d (low oxic), > 693 (anaerobic). The sorption of MCPA was 44 l/kg (soil) resp. 47 l/kg (sediment) when a mixture of aldicarb, simazine, mecoprop and MCPA was used. Other pesticides did not show this effect. Remarks Incubation experiment: unusual incubation method; value not used.
Ohyama H. (1977) MCPA addendum thioethyl. Vol. 3 B7 – Metabolism and degradation of phenothiol Description Degradation of phenotiol (MCPA-thioethyl) was studied in three paddy soils under both upland conditions and flooded, at 30 °C. MCPA-thioethyl rapidly degraded and MCPA was found to be the major

metabolite under flooded conditions. Data for upland conditions not reported. No half-life for MCPA reported.

Remarks

Soils are not representative of temperate regions.

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